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LABORATORY PROTOCOLS FOR EVALUATING THE FATE OF ORGANIC CHEMICALS IN AIR AND WATER

by

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FOREWORD

Environmental protection efforts are increasingly directed towards prevention of adverse health and ecological effects associated with specific compounds of natural or human origin. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Technology Development and Applications Branch develops appropriate transport and transformation measurement protocols, source information, and environmental data bases for application to models that assess toxic chemical exposure.

Delineation of the environmental pathways followed by potentially harmful chemicals is a key element in predicting the effects of pollutants before extensive damage occurs. This report presents procedures (or protocols) for obtaining rate and equilibrium constant data for use in evaluating some of the important pathways of chemicals in aquatic and atmospheric environments.

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ABSTRACT

Laboratory test procedures (or protocols) have been developed to provide data useful in evaluating the environmental fate of organic compounds in natural aquatic systems and in the atmosphere. Screening-level protocols are described to estimate rate constants for hydrolysis, photolysis, oxidation, biotransformation, and volatilization processes in natural aquatic systems; a screening protocol for measurement of partition coefficients for sorption of organic chemicals to sediments is also described. Detailed test protocols have been developed for the hydrolysis, photolysis, volatilization, and sediment-sorption processes to obtain more accurate and precise data for use in environmental assessments applied to aquatic systems. Screening and detailed test protocols are described for estimating rate constants for the atmospheric photolysis and oxidation of organic compounds. For each process, the theory and the present state of knowledge regarding the environment are reviewed, and some common methods currently in use are critically evaluated.

This report was submitted in fulfillment of Contract No. 68-03-2227 by SRI International under the sponsorship of the U.S. Environmental Protection Agency. The report covers the period from October 1977 to January 1980. After peer review, the report was revised under EPA Contract No. 68-03-2981, October 1981.

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Dr. Dale G. Hendry, the author of one chapter in this report and coauthor for two other chapters, died in June 1981. Dr. Hendry's death is a personal as well as a professional loss to his coworkers at SRI and to his colleagues in the scientific community. His research in oxidation chemistry, photochemistry, and atmospheric chemistry was instrumental in developing the procedures and background sections in this report.

CHAPTER 1. INTRODUCTION

The Toxic Substances Control Act of 1976 (P.L. 94-469) requires that the EPA evaluate all new chemicals for their possible adverse effects on the environment before manufacture and use are permitted. The act also provides that the manufacturers of new chemicals provide the EPA with laboratory and other test data on fate and effects for specific chemicals that may constitute a possible hazard to a biological population. To be useful to the EPA, test data must be developed under conditions that allow meaningful interpretation in the context of environmental transport and transformation processes.

There is general consensus among experienced investigators that, at this time, predictions of environmental pathways for chemicals are most reliably and economically obtained from laboratory evaluation of the physical, chemical, and microbiological processes important in the environment. With the appropriate data, this approach can provide information on the fate of specific chemicals in a wide variety of aquatic and atmospheric environments. Therefore, it is essential that the EPA develop guidelines and specific procedures for carrying out laboratory tests for use in fate assessment.

This report was prepared by SRI International (formerly Stanford Research Institute) for EPA under contract No. 68-03-2227 to evaluate existing test procedures and recommend test protocols for the following environmental processes:

Hydrolysis in water
Photolysis in water
Oxidation in water
Atmospheric chemistry
Aquatic biodegradation
Volatilization from water
Sorption of organics on sediments.

1.1 GENERAL CONSIDERATIONS

In individual sections of this report, we discuss kinetics, test methods, and recommendations for test protocols for each of the seven specific chemical or physical processes listed above. This section outlines the relationship between laboratory experiments and environmental processes and some basic requirements for laboratory test procedures intended to be used for environmental assessment.

The foundation for use of laboratory data for environmental assessment is based on the following assumptions:

- The rate of transformation or transport of a chemical in or from an environmental system is the sum of the rates of known individual chemical, physical, and biological processes.*
- The rate or equilibrium constants for these processes can be measured independently in the laboratory.
- The laboratory data for individual processes can be integrated and extrapolated to the appropriate set of environmental conditions using simple or computer models.

These same assumptions are also implicit in the use of models to describe photochemical smog, agricultural run-off, and other environmental processes with varying degrees of complexity. The success of any effort to model or assess the transport and transformation of a chemical in the environment thus depends on two factors: (1) availability of reliable rate or equilibrium data, usually developed in the laboratory, and (2) a reliable method for using such data in an environmental assessment.

This second factor refers specifically to extrapolation or scaling methods that accurately combine environmental variables, such as pH, wind velocity, or microbial cell count, with the process affected by the variable. Since a specific equilibrium or rate process can be measured quite accurately usually to within ± 10%, whereas values of environmental variables can vary dramatically and are rarely known to within more than a factor of two, the accuracy of fate estimates is usually limited by the accuracy of the environmental descriptors, not the laboratory data.

For example, the efficiency of a photochemical process can be measured fairly easily with an accuracy of ± 10% in the laboratory and applied to the calculation of the rate of photolysis in sunlight at a specific time and location using sunlight intensity data from the literature. However, the photolysis in sunlight is variable and uncertain owing to random fluctuations in light intensity from cloud cover, backscatter, and light absorption by other chemicals. In this example the net rate of the process follows a relation

---

*This assumption implicitly neglects interactive processes that would accelerate or retard a specific transport or loss process; their importance probably is not great in most environmental systems.

$$\text{Rate} \propto \phi I$$

where ϕ is the efficiency of the process (quantum yield) and I is the intensity of sunlight. Since the standard error ratio in rate is related to the sum of standard error ratios for ϕ and I (section 3.6.8) there is a significant advantage in measuring ϕ as accurately as possible in the laboratory, to the point where the error in ϕ is reduced to about one-fifth the error in I.

1.2 CRITERIA FOR SELECTION OF SUITABLE TEST METHODS

Although many experimental procedures have been described to measure rate and equilibrium constants for processes analogous to those found in the environment, for several reasons most procedures are inapplicable for developing data useful for fate assessment. One reason is that some procedures give only qualitative information about the process and thus can be used only to judge whether the reaction occurs or not. Another reason is faulty design of the experimental procedure, which prevents control of some important variables and hence gives data that are affected by some other, unsuspected and more rapid process. An example of this situation is found in measurements of loss of a highly insoluble chemical from water at elevated temperature, where the loss is thought to be caused by hydrolysis but actually is caused by volatilization.

A third reason is that some procedures are used in the laboratory under conditions for which no satisfactory extrapolation is possible to a specific environmental situation. A good example is the measurement of the rate of biotransformation of a chemical dissolved in a natural water, and where only the loss of chemical or evolution of carbon dioxide is monitored. In this case, the necessary data to quantitatively link these results to an aquatic environment — for example, information on the lag phase and cell counts — are lacking and no reliable extrapolation is possible.

Thus, the scientific criteria for judging the suitability of a test procedure for environmental assessment are the quantitative character of the data, the use of proper controls to ensure the applicability of the data for the intended process, and the availability of reliable scaling or extrapolation procedures.

Apart from the purely scientific validity of specific laboratory tests, the generality and complexity or sophistication of tests must also be considered in evaluating available methodologies, especially if such tests are intended as protocols for regulatory use. Thus, a test procedure that requires use of a complex and expensive Fourier transform magnetic resonance spectrometer is not likely to be adopted as a protocol for industry-wide use. Preferred test methods are those generally carried out by experienced laboratory personnel with instruments commonly found in well-equipped analytical and physical chemistry laboratories. Each procedure must be evaluated for the balance between speed, accuracy and cost.

To achieve both economy and reliability in environmental assessment, we need to consider the use of screening tests in exposure assessment. Usually, only one or two environmental processes control the persistence and fate of a specific chemical in aquatic or atmospheric environments. Thus in many cases, testing costs can be significantly reduced through rapid screening tests designed to give approximate values of rate constants or equilibrium constants for comparison of competing rate processes in simple assessment models.* Processes not significant in this assessment usually can be eliminated from further evaluation, with savings in cost and simplification of subsequent detailed assessment. In subsequent sections of this report, we evaluate and recommend both screening and detailed tests for each process.

In the preparation of these protocols, we have assumed that a valid analytical method is available for analysis of the chemical being tested. Analytical procedures and techniques are usually selected by the equipment available and by the properties of the chemical (that is, susceptibility to analysis by flame ionization or electron capture detectors, or absorbance, etc.) If special analytical devices or procedures are used, the experimental approach should be carefully examined to determine whether the protocol is affected. It is also expected that suitable controls (or blanks) will be performed for each protocol with each chemical to identify any adventitious processes that would introduce artifacts into the data obtained. Control experiments are designed with considerations of both the fundamentals of the process which the protocol is intended to quantify, and the adventitious processes which may complicate the experimental data.

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*By a simple model we mean a well-mixed single compartment in which the overall rate of transformation of the chemical is easily calculated using the simple relation

$$k_t = k_1 + k_2 + \ldots . k_n$$

where k_t is the observed rate constant and k_1, k_2, and k_n are simple first-order rate constants for individual environmental processes. Sorption may not be included in this preliminary assessment.

CHAPTER 2. HYDROLYSIS IN WATER

by

T. Mill, W. R. Mabey, and D. G. Hendry

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2. HYDROLYSIS IN WATER

2.1 INTRODUCTION

The deliberate and accidental introduction of many hundreds of different organic chemicals into major streams and rivers in this country is well documented. Reactions of some of these chemicals with the water is one possible process that transforms them into new structures with properties that are very different from their precursor molecules. Therefore data on the rate constants for hydrolysis of chemicals having a hydrolysable function are necessary to evaluate the importance of hydrolysis as a dominant pathway for transformation of some chemicals.

This section evaluates methods available for obtaining the data needed to calculate rates of hydrolysis or half-lives under conditions found in aquatic systems. From these methods we have selected a few to use as screening and detailed test protocols for hydrolysis.

2.2 SUMMARY

Screening and detailed test protocols for hydrolysis of chemicals in water have been prepared to enable an investigator to select chemicals with half-lives of one year or less and estimate hydrolysis rate constants and half-lives for most chemicals at any environmental pH and temperature. Only chemicals with half-lives of less than one year are considered for detailed study.

The test protocols are based on a large body of experimental data for hydrolysis together with detailed kinetic analysis of the process. The recommended test protocols meet the criteria of quantitation, accuracy, and applicability to experimental systems and are cost-effective and simple to use for a wide range of chemical structures. Background data on hydrolysis kinetics and a review of studies of hydrolysis rates of some pesticide chemicals in buffered and natural waters are presented to demonstrate that, in most natural waters, only pH and temperature affect rates of hydrolysis. All investigations to date show that hydrolysis rates in buffered and natural waters are the same within experimental error.

2.3 CONCLUSIONS

Present knowledge of the theory and experimental aspects of hydrolysis reactions provide a sound basis on which to propose hydrolysis protocols. The recommended protocols for screening and detailed studies represent a balance between the economic need to minimize laboratory work and the scientific requirements for sufficient and accurate data. The screening protocol can be used to identify chemicals that have half-lives of less than a year. The detailed protocol can be used to determine data necessary to calculate rate constants and half-lives for hydrolysis at any pH and temperature encountered in aquatic environments.

2.4 RECOMMENDATIONS

The protocols should be tested in the laboratory for applicability to several chemicals of environmental concern. Initial studies should include chemicals from classes with known pH-rate profiles, such as esters or alkyl halides. A dibutyl phthalate and ethylene dibromide would be two such chemicals.

For chemicals in classes whose pH-rate profiles are unknown, we recommend that general pH-rate profiles be established for the class of compounds. Data from protocols carried out for specific chemicals can then be referenced to the known profiles.

Validation of laboratory tests should be carried out using limited field tests (enclosed ponds) and a simple model.

2.5 SCREENING TESTS

2.5.1 Purpose

This screening protocol is intended to identify chemicals with half-lives of less than 1 year during hydrolysis at 25°C for simple environmental fate assessment applications.

2.5.2 Detailed Procedure

Solutions should be prepared using sterile, pure water and Reagent Grade (or purer) chemicals. Buffer solutions should be prepared according to the following procedures:

- pH 3.0: 50 ml of 0.10 M $KHC_8H_4O_4$ is mixed with 22.3 ml of 0.10 M HCl and diluted to 100 ml.
- pH 7.0: 50 ml of 0.10 M KH_2PO_4 is mixed with 29.1 ml of 0.10 M NaOH and diluted to 100 ml.
- pH 11.0: 50 ml of 0.05 M $NaHCO_3$ is mixed with 22.7 ml of 0.100 M NaOH and diluted to 100 ml.

- For each chemical being tested reaction mixtures should be prepared in each of the three buffer solutions without the use of heat. The chemical should be at a concentration less than one-half its solubility in water and at less than 10^{-3} M. If necessary, 1 volume percent acetonitrile may be added as cosolvent if the chemical is too insoluble in pure water to permit reasonable handling and analytical procedures. Acetonitrile is stable enough up to 80°C to permit its use as a cosolvent; above 80°C, 1% ethanol in water is the recommended solvent for hydrolysis tests.
- Sealed ampoules or stoppered (no grease) volumetric flasks containing the reaction mixtures should be placed in a constant temperature bath at 25 ± 1°C in the dark. Solutions should be analyzed for the concentration of chemical and at t = 0, 44 and 88 hr. Wherever possible, an analytical procedure should be used that provides a precision within ± 5%.

2.5.3 Criteria for Screening Test

The solution at pH 7 is both a control solution and one point on the pH rate profile curve (see Section 2.6.2). If no loss of chemical is noted in 88 hr in this solution, any losses noted in the solutions at pH 3 and 11 are probably due to hydrolysis. Significant loss of chemical from the pH 7 solution may indicate the intervention of some other loss process such as sorption, volatilization, or biological transformation. These possibilities should be checked before proceeding with additional analyses or calculations (see Section 2.6.3). If hydrolysis does occur at pH 7 and if more than 75% of the chemical has hydrolyzed after 2 hr, the hydrolysis half-life will be less than 1 hr. In this case the chemical will not persist in the aquatic environment, and detailed hydrolysis studies are then not necessary.

Providing that the control solution data are satisfactory, the loss rates from the pH 3 or 11 solutions may be interpreted in a straightforward manner; if more than half the initial concentration of chemical has hydrolyzed at either pH 3 or 11, or both, in 88 hr, the chemical is expected to have a half-life of less than 1 year at pH 5 or 9, respectively, or both (see Section 2.7). As a check on the reliability of the percent loss of chemical at 88 hr, the loss at 44 hr should be more than 29% if the half-life is less than 1 year.

The basis for this screening study is that most chemicals hydrolyze at pH 3 or 11 at rates that are one hundred times as fast as at pH 5 or 9, respectively; thus, a measured half-life of less than 88 hr at pH 3 or 11 is equivalent to a half-life of less than 8800 hr or one year at pH 5 or 9, respectively. If more than 75% of the chemical has hydrolyzed after 2 hr, the half-life is less than an hour.

If the environmental hydrolysis half-life is found to be less than a year, detailed hydrolysis studies are recommended for the chemical. This recommendation is based on a screening test, however, and detailed studies may not be necessary if other screening data show the chemical has low toxicity or is more rapidly transformed by other processes.

2.5.4 Rationale

The screening test described above is a simple, rapid procedure for qualitatively evaluating hydrolysis rates and half-lives; it requires common laboratory chemicals and equipment and minimal time, assuming that a valid method is available or can be developed for analysis of the chemical in water. The test is designed to identify those chemicals that have environmental half-lives of more than or less than a year at pH 5 or 9 at 25°C. These are limiting conditions encountered in most freshwater systems because at pH 5 or 9, acid- and base-promoted reactions can have significant rates, and 25°C is higher than the average temperature of most aquatic systems. Thus, this screening test is conservative in subjecting a maximum number of compounds to detailed studies.

2.5.5 Scope and Limitations

The screening test for hydrolysis at pH 3, 7, and 11 is designed to separate chemicals into three groups: those with hydrolysis half-lives (1) greater than one year at pH 5 and/or pH 9, (2) less than a year but more than 1 hour at pH 5 and/or pH 9, and (3) less than 1 hour at pH 7. The test procedure is simple, but correct interpretation requires that the chemical be dissolved in water and have no functional group that ionizes in the pH region 3 to 11.

2.6 DETAILED TESTS

2.6.1 Purpose

The objective of this test protocol is to provide a uniform procedure for accurate measurement of rates of hydrolysis and estimation of rate constants (k_h) under conditions that will enable the investigator to estimate a rate constant for hydrolysis at any pH and temperature commonly encountered in environmental water bodies--usually pH 5-9 and 5-30°C. Therefore, some information concerning the dependence of k_h on both pH and temperature must be developed from which to estimate values of the acid, base and neutral hydrolysis rate constants, k_A, k_B, k_N and their Arrhenius activation parameters.

2.6.2 Estimation of Half-Life from Screening Studies

Screening studies provide a basis for a quick estimate of the lifetime (and rate constant of the chemical in hydrolysis) at any pH. From the loss of chemical measured at 88 hr at any pH, the half-life is

$$t_{\frac{1}{2}}/\text{hr} = (88) \times 0.69/\ln(C_o/C_{88})$$

and the rate constant is

$$k_h/\text{hr}^{-1} = \ln(C_o/C_{88})88$$

where C_o and C_{88} are the concentrations of chemical at time 0 and 88 hr, respectively.

If hydrolyses observed at pH 3 and 11 are due only to the acid and base-promoted reactions, respectively (Section 2.7.2), then the half-life at any intermediate pH can be estimated by using the multiplication factors shown below:

Acid Reaction pH	Multiply Half-life By	Base Reaction pH
3	1	11
4	10	10
5	10^2	9
6	10^3	8
7	10^4	7

This interpolation tends to give estimated half-lives that are too long because it assumes that no other hydrolysis process contributes to the overall rate; the half-lives estimated in this way are useful only in planning detailed experimental studies. As an additional aid to selecting conditions where the reaction rate is conveniently rapid, the half-life at any temperature may be approximated by assuming that the measured half-life will double (or be halved) for each 10°C decrease (or increase) in temperature.

2.6.3 Evaluation of Rate Constants for Hydrolysis

The rate of hydrolysis should be measured at pH 3, 7, and 11 at the same temperature, preferably 25°C, using the procedure described in Section 2.5. Rates of hydrolysis should be fast enough so that 60-70% hydrolysis is effected in not more than several weeks' time. For these experiments, temperature control should be ± 0.1°C or better. Each reaction mixture should be analyzed at regular intervals to provide a minimum of six time points between 20% and 70% hydrolysis of the chemical. Control experiments are also needed as indicated in Section 2.5.1. If hydrolysis is too slow at 25°C to conveniently follow the reaction to high conversion in several weeks but still rapid enough to measure 20-30% conversion, the accuracy of the data will be improved if more data points are taken between 10 and 30% conversion; fifteen to twenty time-points are preferable. If the reaction is too slow to measure a significant reaction in several weeks, a higher temperature should be used; see Section 2.6.4 below for procedures for temperature extrapolation.

To demonstrate that the hydrolysis reaction is a first-order reaction over the interval of 10-60% conversion, two concentrations of chemicals should be used that differ by about a factor of ten.

Rate constants for hydrolysis (k_h) can be evaluated from the concentration-time data in several ways. The simplest procedures are (1) to plot the log of concentration of chemical against time using semi-log paper (the best straight line through the points will have a slope equal to $-k_h/2.3$), and (2) to more precisely and accurately evaluate k_h, fit the data by linear regression analysis to the equation $\ln(C_t/C_o) = -k_h t$, where C_t and C_o are the concentrations of chemical at times t and 0.

Marked curvature in a plot of log C versus time or a low correlation coefficient indicates that a non-first order process is taking place and additional experiments may be necessary.

Since k_h is the composite rate constant (see Section 2.7.2).

$$k_h = k_A(H^+) + k_N + k_B(OH^-) \tag{2.1}$$

The values of k_A, k_B, and k_N are readily obtained from the values of k_h measured at pH 3, 7, and 11:*

$$k_A = 10^3\left[k_{h(3)} - k_{h(7)} + 10^{-4}k_{h(11)}\right] \tag{2.2}$$

$$k_B = 10^3\left[k_{h(11)} - k_{h(7)} + 10^{-4}k_{h(3)}\right] \tag{2.3}$$

$$k_N = k_{h(7)} - 10^{-4}\left[k_{h(3)} + k_{h(11)}\right] \tag{2.4}$$

The overall rate of hydrolysis and the composite rate constant k_h may be calculated at any pH by using eq 2.1 and the values of k_A, k_B, and k_N. Eq 2.1 also shows that if k_A or k_B are less than 10 k_N, the reaction will be pH independent from pH 3 to 7 or 7 to 11, respectively. Under these conditions, eqs 2.2 to 2.4 predict that k_A and $k_B < 0.1\ k_N$; that is, the equations are not sensitive enough to detect the true values of k_A or k_B. This limitation is not serious, however, since as a practical matter, neither process will contribute more than 1% to the overall rate in this pH region.

For example, if the values of k_h at pH 3, 7, and 11 are assumed to be 2.1×10^{-1}, 1×10^{-2}, and 2×10^{-2} hr^{-1}, respectively, solving for k_A, k_N, k_B using eqs 2.2 to 2.4 gives $k_A = 2 \times 10^2$ M^{-1} hr^{-1}, $k_N = 1 \times 10^{-2}$ hr^{-1}, and

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*See Appendix 2.A for general solution to eq. 2.1 for any three pH values.

$k_B = 10\ M^{-1}\ hr^{-1}$, respectively. The value of k_h at say pH 8.7 can be calculated by substitution in eq 2.1 together with the values of H^+ and OH^- at pH 8.7 (at 25°): $H^+ = 2.0 \times 10^{-9}$ M; $OH^- = 5.0 \times 10^{-6}$ M

$$k_h = 2 \times 10^{2}\ (2 \times 10^{-9}) + 1 \times 10^{-2} + 10\ (5 \times 10^{-6}) = 1.0 \times 10^{-2}\ hr^{-1}$$

2.6.4 Exact Temperature Dependence Measurement

Many chemicals hydrolyze too slowly at 25°C to allow measurement of their rates conveniently in less than a few months. In these cases some elevated temperature must be chosen to provide rates that are rapid enough to be measured with accuracy and convenience but not so high as to cause other problems such as volatilization or loss of solvent. Rate constants k_h, k_A, k_N, and k_B evaluated at an elevated temperature must be extrapolated to 25°C or some lower temperature to be useful in environmental assessment. The temperature dependence of any discrete hydrolysis process may be expressed by the Arrhenius relation[‡]

$$k = Ae^{-E/RT}$$

where A is the entropy term, E is the activation energy, and R is the gas constant 1.987 cal deg^{-1} mol^{-1}. Between any two temperatures, the following relationship holds

$$\ln\left(\frac{k_{T_1}}{k_{T_2}}\right) = \frac{E}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

At a pH where hydrolysis occurs by a combination of two or more processes, temperature dependence is more complex

$$k_h = k_A[H^+] + k_N + k_B\,[OH^-] = A_A e^{-E_A/RT}[H^+] + A_N e^{-E_N/RT} + A_B e^{-E_B/RT}[OH^-]$$

Since A and E for each process are usually different, no analytical solution to the composite equation is possible. Moreover, although approximations to the temperature dependence of k_h at one pH are possible and useful in limited ways (see below), the exact solution of the temperature dependence relation for each process--in which values of E_A, E_B, E_N, A_A, and A_N are calculated from the data obtained at several pH values and temperatures--is the most satisfactory method for calculating k_h at any other temperature and pH.[*] To evaluate E and A for each process requires knowing the rate constants for the three processes k_A, k_N, and k_B at two or more temperatures; from these data and the Arrhenius relationship, values of A and E for each process can usually be calculated and used to calculate rate constants for hydrolysis at other temperatures and pH values of interest for environmental assessment.

[‡] Temperature is in degrees Kelvin.

[*] Another form of the temperature dependence relationship is used in Section 2.6.8 and Appendix 2.B that does not require explicit calculation of E and A, but both procedures require separation of k_h into the constituent rate constants k_A, k_B, or k_N.

To determine the temperature dependence, rate constants k_h are measured at pH 3, 7, and 11[*] at (where possible) 25°C and two higher or lower temperatures (controlled to ± 0.1°C) at least ten degrees apart. k_h is evaluated and k_A, k_B and k_N are calculated from k_h at each temperature using eqs 2.2 to 2.4. A and E are estimated for each process by plotting log k versus 1/T and taking the best straight line through the three data points, or by fitting the data by regression analysis to the equation $\ln k = A - E/RT$.

For example, the rate of hydrolysis of an ester was assumed to have the following values of k_h at 25°, 40°, and 55°C, and at pH 3, 7, and 11:[‡]

Temp °C	k_h/sec^{-1} pH 3	 pH 7	 pH 11
25	3.00(-7)	1.12(-7)	1.20(-4)
40	1.58(-6)	7.98(-7)	3.17(-4)
55	7.81(-6)	4.95(-6)	7.71(-4)

(Values in parentheses are exponents of 10.)

Equations 2.2 to 2.4 were used to calculate values of k_A, k_N, and k_B at each temperature:

Temp °C	k_A, (sec^{-1})	k_N, $M^{-1}\ \text{sec}^{-1}$	k_B, $M^{-1}\ \text{sec}^{-1}$
25	2.00(-4)	1.00(-7)	1.20(-1)
40	8.14(-4)	7.66(-7)	3.16(-1)
55	2.86(-3)	4.87(-6)	7.66(-1)

Regression analysis on the three sets of three rate constants at three temperatures gave values of E_A, E_N, and E_B: $E_A = 17.224$, $E_N = 25.156$, and $E_B = 12.000$ kcal mol^{-1}. Corresponding values of log A are: $\log A_A = 8.9355$, $\log A_N = 11.4503$, and $\log A_B = 7.88016$ in units of $\text{mol}^{-1}\ \text{sec}^{-1}$ or sec^{-1}.

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[*] pH of buffered solutions should be checked at temperature and adjusted to the correct pH if necessary (Section 2.7.2).

[‡] Experimental errors are deleted from this example; estimation of the probable errors in this procedure are given in Section 2.6.8 on Error Analysis. These kinetic data were selected to illustrate the use of the optional estimation methods and are not derived from any actual measurements.

These values of A and E can be used to recalculate values of k with a 4% error and to calculate new values of the rate constant k_h. For example we can calculate k_h and the half-life for this ester at 15°C (288°K) and pH 5.2.

$$\log k_A(15°C) = 8.9355 - 17.224/\theta = -4.1511$$

$$k_A = 7.06 \times 10^{-5}\ M^{-1}\ sec^{-1}\ (\theta = 4.57T)$$

$$\log k_N(15°C) = 11.4503 - 25.155/\theta = -7.6621$$

$$k_N = 2.177 \times 10^{-8}\ sec^{-1}$$

$$\log k_B(15°C) = 7.8802 - 12.000/\theta = -1.2372$$

$$k_B = 5.791 \times 10^{-2}\ M^{-1}\ sec^{-1}$$

At pH 5.2 $[H^+] = 6.3 \times 10^{-6}$ M and since at 15°, $K_w = 4.57 \times 10^{-15}$ (see Section 2.6.2), $[OH^-] = 7.26 \times 10^{-10}$ M.

$$k_h(15°) = 7.06 \times 10^{-5}(6.3 \times 10^{-6}) + 2.177 \times 10^{-8} + 5.79 \times 10^{-2}(7.26 \times 10^{-10})$$

$$k_h(15°) = 2.181 \times 10^{-8}\ sec^{-1}$$

$$t_{1/2} = 368\ \text{days}$$

2.6.5 Approximate Measurements of Temperature Dependence

The foregoing procedure may be approximated at a fixed pH by assuming that the temperature dependence of k_h, which can be measured to give an apparent activation energy, E_h, is linear with $e^{-1/T}$ and can be used to extrapolate k_h to a new temperature at the same pH. However, since k_h is not actually linear in $e^{-1/T}$, owing to the presence of more than one kind of process, the value of E_h will vary with the temperature range used to calculate its value. Thus, for example, in the hydrolysis of the above ester at pH 7, where the base-promoted reaction makes a significant contribution to the overall rate, values of E_h change from 15.04 to 16.19 kcal mol^{-1} between 25 and 55°C. Nonetheless, for short temperature intervals, the use of an E_h for extrapolating k_h leads to only small errors. A comparison is obtained by calculating the value of k_h at 15°C* and pH 3 by using (1) the exact solution given in 2.5.2.4 and (2) the approximation of E_h.

(1) $k_h(15°)$ at pH 3 $= 7.06 \times 10^{-8} + 2.18 \times 10^{-8} + 5.79 \times 10^{-13}$

$= 9.24 \times 10^{-8}\ sec^{-1}$

(2) E_h calculated from the values of E_h at pH 3 and 25 and 55° is 21.10 kcal mol^{-1}.

---

*Temperature measurements are assumed to be accurate to ± 0.1°C but actual temperatures are cited to two significant figures only.

From E_h and k_h at 25° and pH 3

$$\ln\left(k_h(15°)\right) = \left(\ln k_n(25°)\right) R/E_h\left(\frac{1}{298} - \frac{1}{288}\right)$$

$$= 3.00 \times 10^{-7}/3.446$$

$$k_h(15°) = 8.70 \times 10^{-8} \text{ sec}^{-1}$$

The error in using the approximation is only 20% over this range; thus, for many temperature measurements made close to 25°C and not over 60°C, the use of E_h for extrapolating to any temperature between 60 and 10°C should give a satisfactory result. However, this approximation method has a serious limitation in that values of k_h cannot be calculated at pH values other than those for which temperature measurements have been made. If measurements have been made, at several pH values and temperatures, then in view of the small amount of additional work needed to calculate the exact value of E for each process from the same data, we recommend using the exact method described in Section 2.6.4.

2.6.6 Rationale

The foregoing detailed procedure is intended to provide accurate kinetic information concerning the effect of pH and temperature on the rate constant for hydrolysis. The procedure requires that close attention be paid to control experiments, temperature and pH regulation, and calculation of individual rate constants from experimental data. Hydrolysis experiments in duplicate are recommended for three pH values and at three temperatures for a minimum of nine experiments. However, some latitude may be possible, particularly for reactions that are rapid at or near 25°C, where extrapolations to other temperatures of concern in assessment procedures are necessarily short.

2.6.7 Scope and Limitations

The foregoing detailed test protocol is intended to provide the quantitative information necessary to estimate rate constants for hydrolysis of most chemicals dissolved in water under a variety of conditions found in aquatic environments. These data will provide estimates of rate constants and half-lives at any pH and temperature of concern for environmental assessment with an accuracy of greater than a factor of two in most cases. Some exceptions should be noted however.

Although many chemicals exhibit limited rate dependence on pH because of the relative unimportance of one or more of the hydrolysis processes in the pH region of prime interest (see Figures 2 through 5 in Section 2.6.2), we recommend that pH measurements always be carried out at three pH values near 3, 7, and 11 in order to check the consistency of the rate data. While intervention of other unsuspected processes can be partly anticipated and minimized through proper experimental design (e.g., sealed and sterile containers to eliminate volatilization and biodegradation, respectively), other chemical processes such as pyrolysis, rearrangement, or elimination may become important for some chemical structures at elevated temperatures.

Initial evidence for such processes will usually be found by formation of different products at high temperatures. Additional evidence for these processes will be found by data analysis for the temperature dependence of k_A, k_N, and k_B; if other processes intervene significantly, these rate constants will probably exhibit nonlinear dependence on $e^{-1/T}$.

The effect of competitive rate processes on hydrolysis rate data will be to increase k at elevated temperatures and decrease k when extrapolated to environmental temperatures; that is, values of E will be increased. If the products are stable the simplest method to correct hydrolysis data for intervention of additional rate processes is to measure only the rate of formation of products from hydrolysis rather than loss of the starting compound. Hydrolysis rate data obtained in this way over a range of pH and temperature should be relatively free of this source of error. However, kinetic analysis of data for formation of products versus time for parallel first-order reactions is different from that for analysis of data for loss of starting chemical versus time or for a simple first-order process (see Appendix 2.C).

Another limitation on the scope of this protocol is found in measurements of the rates of hydrolysis of chemicals that reversibly ionize or protonate in the pH range of interest. Rates of hydrolysis of these compounds will often have unusual pH-rate profiles owing to competition between the reactions of the charged and uncharged forms:

$$H_2O + HAY \rightleftharpoons AY^- + H_3O^+$$

$$AY^- \longrightarrow A + Y^-$$

$$HAY \longrightarrow HA^+ + Y^-$$

The net effect is that the pH-rate profile for HAY will be more complicated than the typical curve and will often have a minimum or maximum, and the exact features cannot be decided *a priori*. Should there be any question concerning the possible importance of this effect in hydrolysis of an ionic chemical having a pK_a or pK_b in the pH region of 3-11, additional measurements should be made to define the pH-rate profile.

2.6.8 Error Analysis

Estimation methods for error analysis of the test protocol are based on certain assumptions concerning the accuracy of specific measurements and the relationships between variables. The test protocols proposed here require measurements of concentrations of the chemical as function of time at 3 pH values and two temperatures that differ by at least 10°.

The error analyses that follow are based on the basic kinetic rate laws cited in Section 2.6.3

$$k_h = \ln(C_o/C)/t$$

$$k_h = k_A[H^+] + k_N + k_B[OH^-]$$

$$k_A,\ k_N \text{ or } k_B = Ae^{-E/RT}$$

Error Analysis for k_h: The estimate of the rate constant k_h is related to the measured variables, concentration and time, by the following regession equation. (Statisticians often designate the estimate of k as $\hat{k}$, but we will ignore the distinction in this discussion.)

$$k_h = \frac{n\Sigma t\ln C - [\Sigma t][\Sigma \ln C]}{n\Sigma t^2 - [\Sigma t]^2} \tag{2.5}$$

where C is concentration of chemical measured at time t. This version of the regression equation does not require that $\ln(C/C_o) = 0$ at $t = 0$; that is, the line is not forced through the origin and any significant departure from the origin indicates bias in values of C at $t > 0$.

The intercept C_o, the concentration at $t = 0$, is obtained from the equation

$$\ln\left(C_o\right) = \frac{1}{n}\Sigma \ln C - k_h\left(\frac{1}{n}\Sigma t\right) \tag{2.6}$$

The preferred measure of error in experiments of this kind is the standard error, σ,* used here in the form σ^2 or the variance. The variance of k_h from n measurements is given by

$$\sigma^2 = \frac{1}{n-2}\left[\frac{n\Sigma[\ln C]^2 - [\Sigma \ln C]^2}{n\Sigma t^2 - (\Sigma t)^2} - (k_h)^2\right] \tag{2.7}$$

Equation (2.7) shows that σ varies with $\frac{1}{t}$ and $\sim \frac{1}{\sqrt{n}}$ and directly with σ(C).

Estimation of Errors in k_A, k_N, and k_B: For the recommended pH values of 3, 7, and 11, equations 2.2-2.4 can be applied; hence, the variances in k_A, k_N, and k_B are given by

$$\sigma^2(k_A) = 10^6\sigma_3^2 + 10^6\sigma_7^2 + 10^{-2}\sigma_{11}^2 \tag{2.8}$$

$$\sigma^2(k_N) = 10^{-8}\sigma_3^2 + \sigma_7^2 + 10^{-8}\sigma_{11}^2 \tag{2.9}$$

$$\sigma^2(k_B) = 10^{-2}\sigma_3^2 + 10^6\sigma_7^2 + 10^6\sigma_{11}^2 \tag{2.10}$$

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*The standard error may be expressed as the standard deviation, (k ± σ), the error ratio, σ/k, or percent error (σ/k) x 100.

where σ_3^2 is σ^2(k_h at pH = 3)

σ_7^2 is σ^2(k_h at pH = 7)

σ_{11}^2 is σ^2(k_h at pH = 11)

Similar relationships hold for other pH values (see Appendix 2.A).

Estimation of Errors in Temperature Extrapolation of Rate Constants k_A, k_N, and k_B: When k_A, k_N, and k_B have been determined at each of two temperatures, T_1 and T_2, extrapolations of k_A, k_N, and k_B to a lower temperature T_0 can be made by the relation

$$k(T_0) = [kT_1]^{(1 + \alpha)}/[k(T_2)]^{\alpha} \tag{2.11}$$

where k may be k_A, k_N or k_B, $T_0<T_1<T_2$ and α depends only on the three temperatures as follows:

$$\alpha = \frac{T_2(T_1 - T_0)}{T_0(T_2 - T_1)}$$

Appendix 2.B gives a detailed derivation of this expression.

The variance of the extrapolated rate constant (k_A, k_N, or k_B) is estimated by the relation

$$\sigma^2[k(T_o)] = \left((1 + \alpha)^2\frac{\sigma^2[k(T_1)]}{[k(T_1)]^2} + (\alpha)^2\frac{\sigma^2[k(T_2)]}{[k(T_2)]^2}\right)[k(T_0)]^2 \tag{2.12}$$

which applies only when $\sigma(k)/k < 0.4$.

Error Analysis for Hydrolysis Kinetic Data: Effect of Reaction Variables on the Error Ratio: Error equation (2.7) has been used to estimate the standard error in k_h at 25°, 40°, and 55° based on the assumption that the standard error in individual concentration measurements for a chemical is ± 4 percent ($\sigma/c = 0.04$) for all data points and that data points are evenly distributed with time for one half-life. Under these conditions, the error ratio σ/k depends in the following way on the number of sample points

$$\sigma/k = 0.20(n - 1)^{\frac{1}{2}}[n(n + 1)]^{-\frac{1}{2}} \tag{2.13}$$

where n is the number of samples. When $n > 5$, the error ratio changes nearly with the square root of the number of sample points. For seven points, $(\sigma/k) = 0.065$; for fourteen points $(\sigma/k) = 0.050$.

The value of (σ/k) is more sensitive to the length of sampling time, since, from eqn 2.7,

$$\sigma^2 \sim \frac{1}{t^2}$$

and

$$\sigma \sim \frac{1}{t}$$

We have assumed that seven data points were used for each rate measurement; as a result $\sigma/k_h = 0.065$ for values of k_h at all pH and temperatures. If two half-lives were used instead of one for the standard reaction time, $\sigma/k = 0.033$; or, analogously, if the precision of the concentration measurement were doubled, $\sigma/k \sim 0.03$.

We have used equations (2.8)-(2.10) to evaluate σ^2 for k_A, k_N, and k_B at 25°, 40°, and 55° based on a value of $\sigma/k = 0.065$ for k_h at all pH values and temperatures (seven points evenly distributed and one half-life). Values of σ^2 were converted to σ/k and are listed below.

Temperature (°C)	σ/k		
	k_A	k_N	k_B
25	0.10	0.07	0.065
40	0.14	0.065	0.065
55	0.20	0.065	0.065

The magnitude of the error found in either k_A, k_N or k_B depends on the relative contributions of each rate process to the measured value of k_h at each pH at one temperature; the relative importance of each process to the total rate changes with temperature (see Section 2.6.4). In this case the larger errors in k_A are due to the relatively small contribution of k_A at all pH values and to its decreasing importance with increasing temperature relative to k_N (lower value of E_A than E_N). Nonetheless, the error ratios (σ/k) often are the same as the error ratio (σ/C) of k_h and close to the error ratio of an individual measurement (0.04).

The effect on the error ratio of changing the measurement strategy was also evaluated. For a set of six concentration data points each having a precision of 4 percent (standard error) but distributed unevenly at one-minute intervals, three at the beginning and three at the end of one half-life, the error ratio for k_A was about two-thirds as large as for the case of evenly distributed data points. Less improvement was found for k_N and k_B where uneven distribution of data points resulted in 25 and 20 percent reductions in σ/k for k_N and k_B, respectively.

Temperature Extrapolation Error: Extrapolation of rate constants at 40° and 55° to 25° were carried out using equations (2.11) and using values of σ^2 from both measuring strategies, (2.12). Values of (σ/k), calculated from σ^2 and k, are listed below

k	σ/k(extrapolated to 25°)	
	even 7 pts	3 pts initial, 3 pts final
k_A	0.37	0.19
k_N	0.16	0.12
k_B	0.16	0.13

The extrapolation of our idealized sets of data to 25° leads to errors ranging from 19 to 37 percent in estimating k_A; similar but smaller errors are obtained for k_N and k_B.

In general, the reductions in errors achieved by using uneven sampling times at the beginning and at one half-life are not large enough to justify recommending the practice; indeed, doubling the total measurement time or reducing the measurement error will reduce the error in k_h more than use of an uneven sampling strategy. Moreover, the need to ensure that the process being measured actually follows a first-order relation provides additional argument for using an even sampling time strategy.

2.7 BACKGROUND*

2.7.1 Definition of Hydrolysis

Hydrolysis refers to a reaction of a compound with water, usually resulting in the net exchange of some leaving group (-X) with OH at a reaction center:

$$RX + H_2O \longrightarrow ROH + HX$$

The mechanism of the reaction may involve a cationic or anionic intermediate, and the hydrolysis rate may be promoted or catalyzed by acidic or basic species, including anion (OH^-) and hydronium ion (H_3O^+ or H^+). The promotion of the reaction by H_3O^+ or OH^- is referred to as specific acid or specific base catalysis, as contrasted to general acid or base catalysis encountered with other cationic or anionic species, respectively.

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*Much of this material has been excerpted from a recent publication on hydrolysis of organic compounds in water (Mabey and Mill, 1978).

For this protocol we consider only specific acid or base catalysis together with the neutral water reaction. The concentration of H_3O^+ or OH^- is directly measured by the pH of the solution (see Section 2.7.2), an easily measured variable for aquatic systems. Although other chemical species can be involved in hydrolysis reactions, their concentrations in aquatic systems are usually quite low and their effects are minimal (see Section 2.7.3).

2.7.2 Kinetics

Rate Laws

The rate law for hydrolysis of chemical RX usually can be put in the form

$$-\frac{d(RX)}{dt} = k_h[RX] = k_B[OH^-][RX] + k_A[H^+][RX] + k_N'[H_2O][RX] \quad (2.14)$$

where k_B, k_A, and k_N' are the second-order rate constants for acid- and base-catalyzed and neutral processes, respectively. Since the concentration of water is nearly constant and much greater than the chemical RX, $k_N'[H_2O]$ is a constant (k_N). The pseudo-first-order rate constant k_h is the observed or estimated rate constant for hydrolysis at a specific and constant pH and temperature. Eq (2.14) assumes that the individual rate processes for the acid, base, and neutral hydrolyses are each first order in substrate. With only a few exceptions, this is the case, and

$$k_h = k_B[OH^-] + k_A[H^+] + k_N \quad (2.15)$$

From the autoprotolysis water equilibrium [eq (2.16)] eq (2.15) may be rewritten as eq (2.17).

$$[H^+][OH^-] = K_w \quad (2.16)$$

$$k_h = \frac{k_B K_w}{[H+]} + k_A[H^+] + k_N \quad (2.17)$$

From eq (2.17), it is evident how pH affects the overall rate: at high or low pH (high OH^- or H^+) one of the first two terms is usually dominant, whereas at pH 7 the last term can often be most important. However, the detailed relationship of pH and rate depends on the specific values of k_B, k_A, and k_N. At any fixed pH, the overall rate process is pseudo first order, and the half-life of the substrate is independent of its concentration:

$$t_{1/2} = 0.693/k_h \quad (2.18)$$

Eq (2.17) is conveniently expressed graphically as three equations--one each for the acid, base, and neutral hydrolysis reactions--in which log k_h is plotted against pH. The curves obtained are especially useful for describing the effect of acid or base on the rate of hydrolysis. Figure 2.1 depicts a typical log k_h versus pH plot for compounds that undergo acid-,

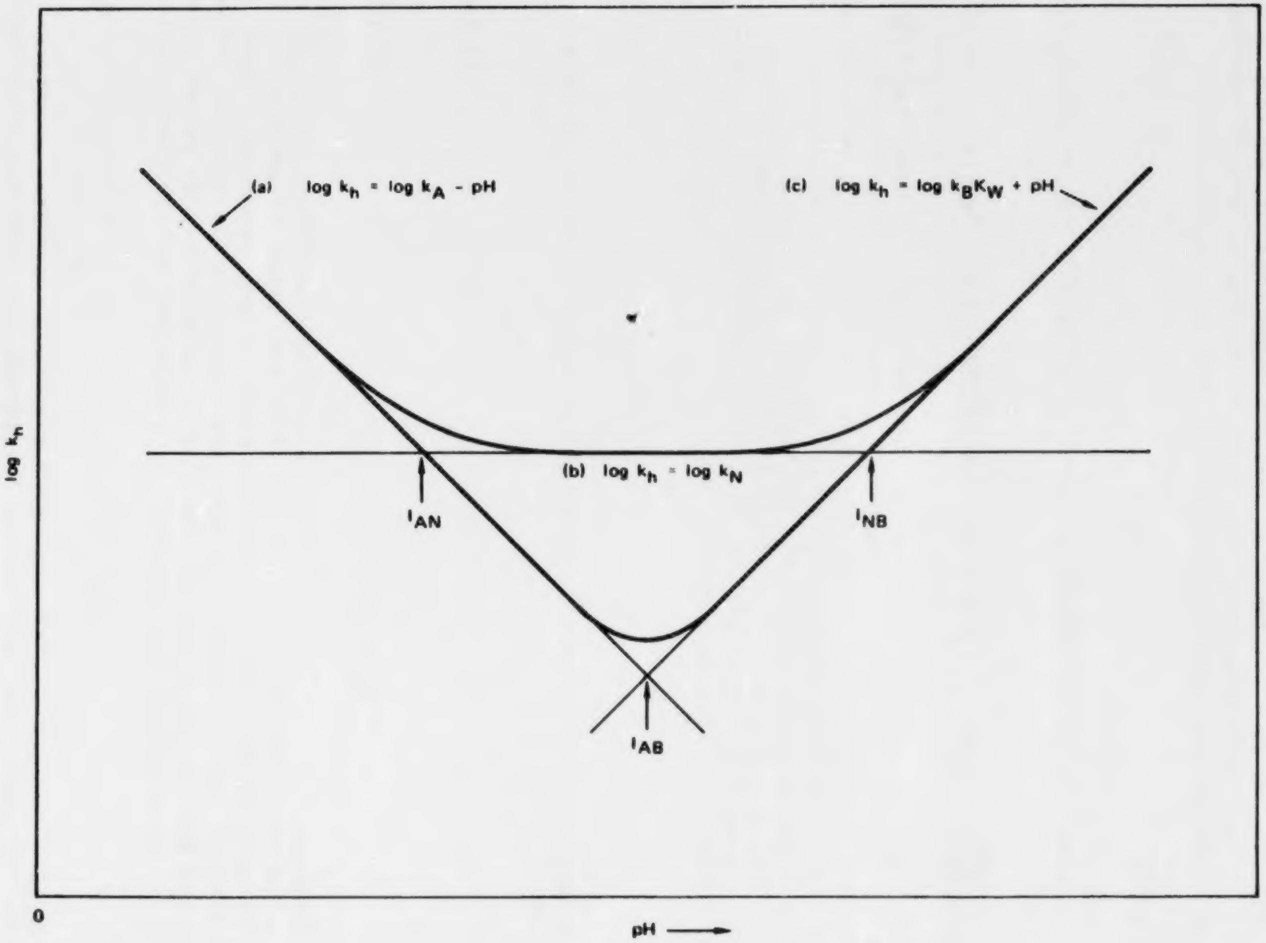

Figure 2.1 pH Dependence of k_h for Hydrolysis by (a) Acid-, (b) Water-, and (c) Base-Promoted Processes

water-, and base-promoted hydrolysis. It is obvious from eq (2.17) that the upper curve in Figure 2.1 is a composite of three straight lines--(a) $\log k_h = \log k_A - pH$; (b) $\log k_h = \log k_N$, and (c) $\log k_h = \log(k_B K_w) + pH$--with slopes - 1, 0, and +1, respectively. The lower curve results when $k_N \ll k_A[H^+]$ and $k_B[OH^-]$.

Most log k_h vs pH curves are found to have one or two areas of curvature corresponding to pH values where two kinds of rate processes contribute to the overall hydrolysis rate. The pH at which the two processes contribute equally to k_h is given by the intercept, I. Thus in Figure 2.1 the intercept I_{AN} corresponds to a value of pH where $k_A[H^+] = k_N$; similarly, I_{NB} corresponds to $k_B[OH^-] = k_N$. In cases where k_A, k_B, or $k_N = 0$, only one intercept is observed. Values of pH corresponding to I may be calculated readily from the values of k_A, k_N, and k_B:

$$I_{AN} = -\log(k_N/k_A) \tag{2.19}$$

$$I_{NB} = -\log(k_B K_w/k_N) \tag{2.20}$$

$$I_{AB} = -[\log(k_B K_w/k_A)]/2 \tag{2.21}$$

Rate Constants

The second-order rate constants k_N', k_A, and k_B for hydrolysis are in the units of concentration^{-1} time^{-1}; for solution kinetics the specific units are commonly molar^{-1} seconds^{-1} (abbreviated M^{-1} s^{-1}, or M^{-1} sec^{-1}). The concentration of pure water is 55.5 M and is essentially unchanged after hydrolysis of dilute solutions of chemicals so that $k_N'(55.5) = k_N$. The units of k_N are then time^{-1} (sec^{-1} or s^{-1}). The units of k_A and k_B are commonly M^{-1} sec^{-1}. Units of k_h, the observed rate constant for hydrolysis, are time^{-1}.

Effect of Structure on Reactivity

pH-rate profiles for several classes of hydrolyzable organic chemicals are shown in Figures 2.2 through 2.5. These curves indicate the relative importance of acid, base, and neutral hydrolysis processes for these chemicals, their absolute rate constants (k_h), and half-lives estimated from k_h, all at 25°C.

Comparison of these curves shows how different structures respond to acid or base promotion: alkyl halides have no acid-promoted reaction, whereas epoxides are nearly insensitive to base-promoted reactions. However, carbonyl derivatives such as esters, amides, or carbamates undergo both acid- and base-promoted processes. Some carbamates and esters also undergo neutral hydrolysis.

Among alkyl halides, k_h (= k_N) spans six orders of magnitude between methyl fluoride and t-butyl chloride, but most epoxides have a k_N very close to 1×10^{-6} sec^{-1}; esters and amides exhibit significant differences in k_h depending on the steric and electronic properties of substituents at the reactive center. In general, esters hydrolyze about 1,000 times as rapidly as

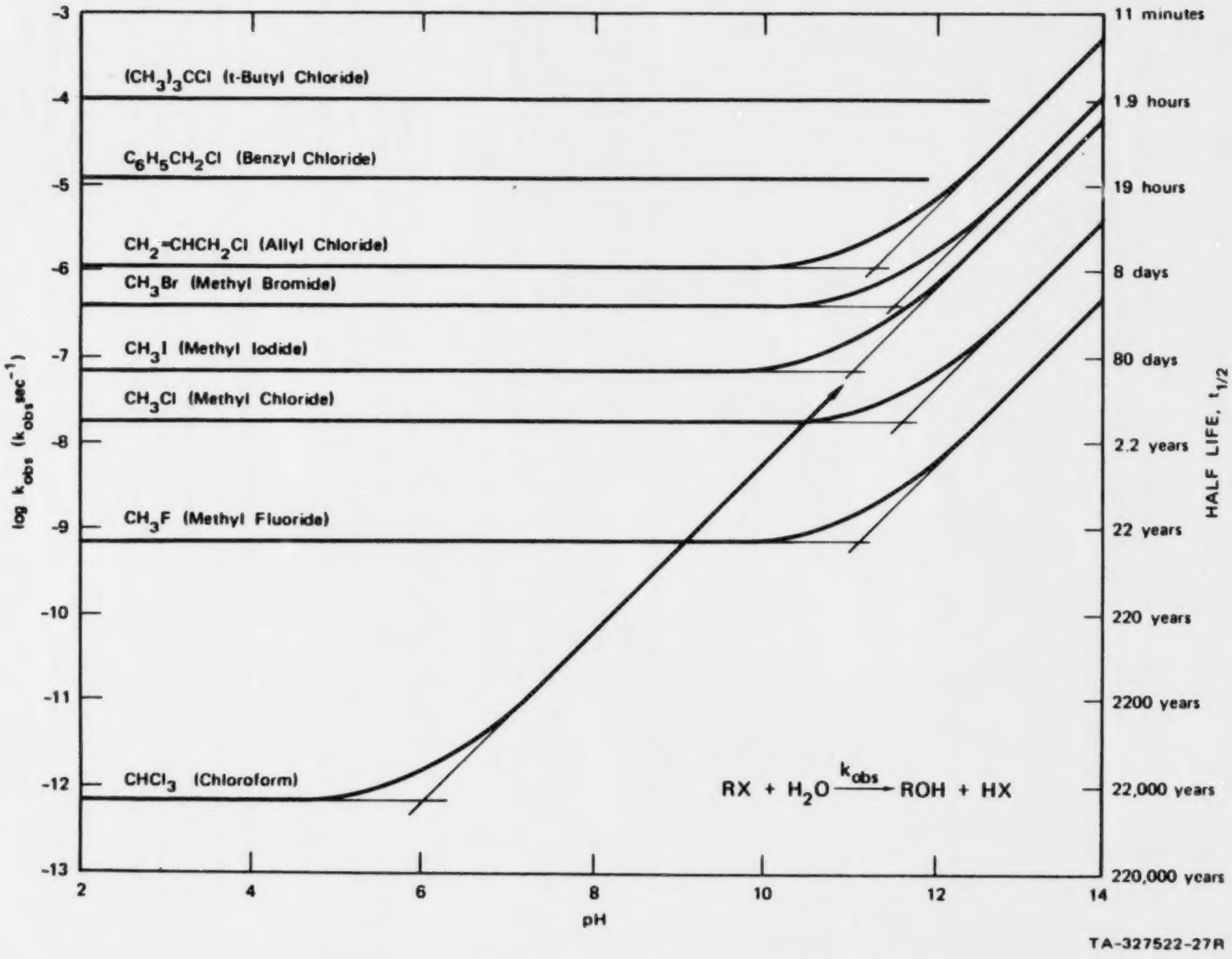

Figure 2.2. Hydrolysis of Alkyl Halides at 25°C.

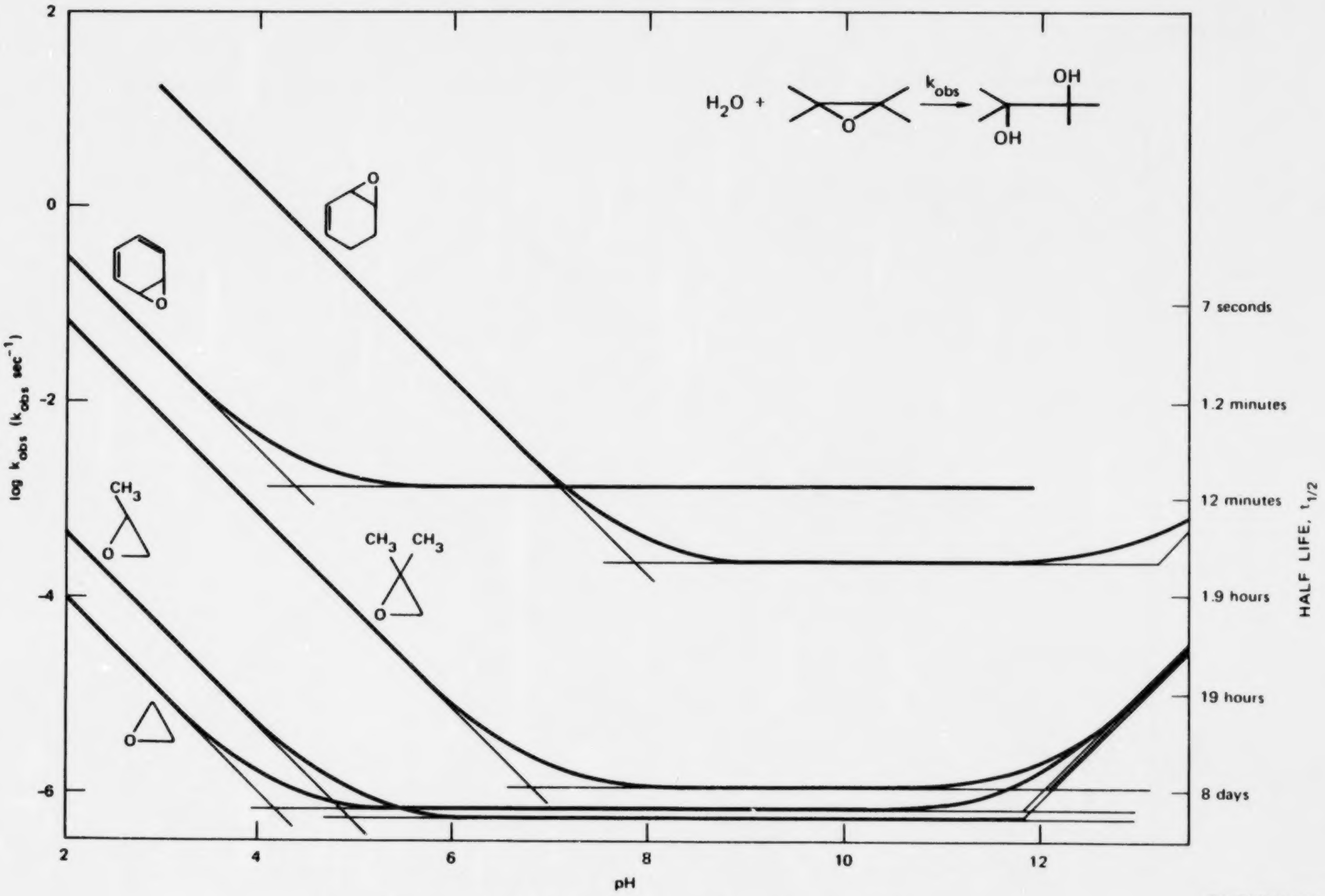

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Figure 2.3. Hydrolysis of Epoxides at 25°C.

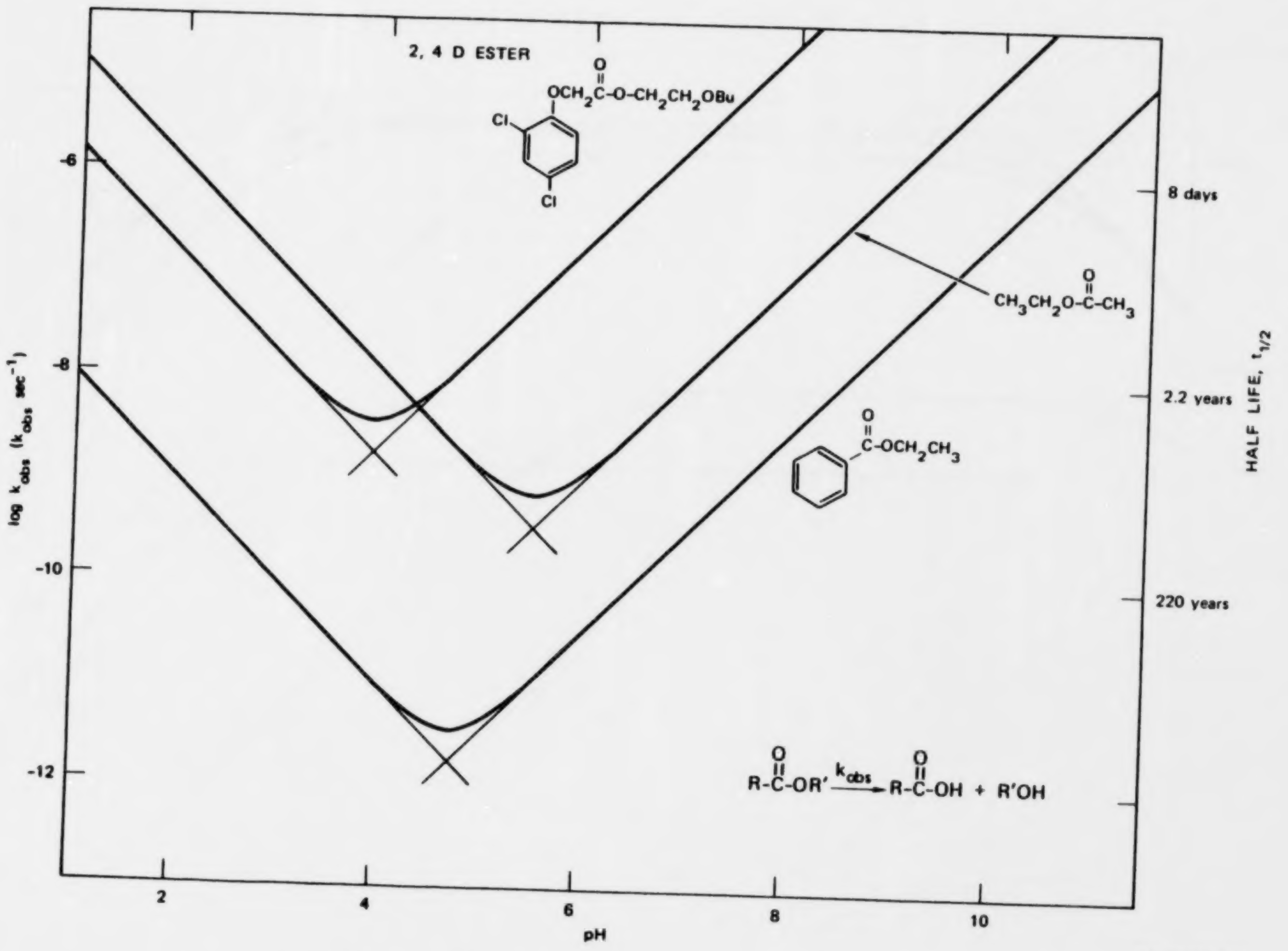

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Figure 2.4. Hydrolysis of Esters at 25°C.

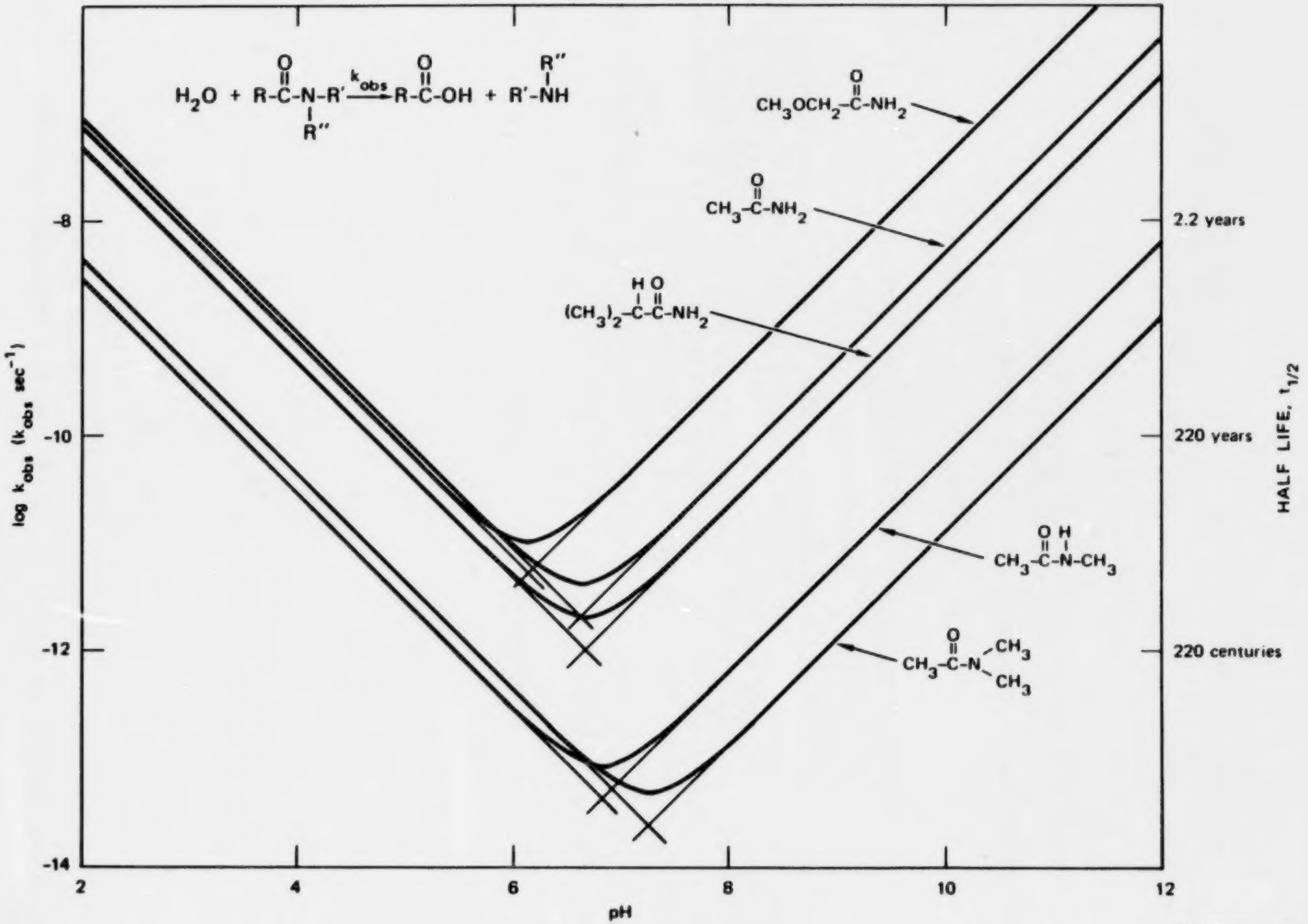

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Figure 2.5. Hydrolysis of Amides at 25°C.

amides at the same pH. Half-lives at pH 7 and 25°C for hydrolyzable chemicals vary from several hundred centuries for some amides to only a few minutes for tertiary halides and aromatic epoxides.

Effect of Temperature

The effect of temperature on the rate constant for a specific hydrolysis process can be expressed in several ways, all of which are variants of the general relation (where T is in degrees Kelvin)

$$\log k = -A/T + B \log T + C \tag{2.22}$$

There is no uniform practice for expressing values of A, B, or C; different investigators have used different versions of eq (2.22), usually in more familiar Arrhenius or absolute rate theory format.

$$\log k = \log A - E/RT \qquad \text{Arrhenius} \tag{2.23}$$

$$\log k = \log(kT_m/h) - \Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R \qquad \text{Absolute Rate Theory} \tag{2.24}$$

We choose to use the Arrhenius form to express the temperature dependence of k because of its simpler form and application. While some accuracy (e.g., heat capacity terms) is gained by using eq (2.22), most experimental data are not precise enough to justify the use of the three-term expression. Units of A are the same as for k, units of E are in kcal/mole or kjoule/mole (1 kjoule = 4.18 kcal), and units of K_w are M^2.

K_w varies with temperature (Harned and Owen, 1958) and follows the relation $\log K_w = \frac{-6013.79}{T} - 23.6521 \log T + 64.7013$

Temperature, °K	$-\log K_w$
273	14.943
283	14.535
293	14.167
298	14.000
303	13.833
313	13.535
323	13.262
333	13.017

A temperature correction should be applied in all calculations involving K_w or $[OH^-]$.

Effects of Ionic Strength and Buffer Salts

The effects of ionic strength on hydrolysis reactions are difficult to predict: they can lead either to rate acceleration or retardation, depending on the substrate, the specific salts, and their concentration. Salt effects of this kind are associated with changes in activity coefficients of ionic or polar species or transition states with significant charge separation; no bond making or breaking is involved in such interactions.

Table 2.1, which lists some effects of different nonnucleophilic salts on the hydrolysis of several kinds of compounds, shows that in most cases rather massive amounts of these salts cause only 30-40% changes in rate constant.

TABLE 2.1. SALT EFFECTS IN HYDROLYSIS REACTIONS

Compound	Salt, M	Solvent, t,°C	k/k_o[a]
t-BuBr	LiBr, 0.1065	90/10 acetone-water, 323	1.44
γ-Butyrolactone	NaCl, 0.51	0.10M HCl, 25	1.08
	$NaClO_4$, 0.40	0.10M $HClO_4$, 25	0.95
CH_3CO_2Et	LiCl, 2.00	0.15M $HClO_4$, 25	1.35
	$NaClO_4$, 2.00	0.15M $HClO_4$, 25	1.00
CH_3CO_2Me	NaCl, 0.100	0.01M NaOH, 35	0.96

[a] k/k_o is the ratio of rates with (k) and without (k_o) salt.

Another effect of nucleophilic added salts is to accelerate the rate of hydrolysis by a general acid- or general base-promoted process (where H^+ or OH^- promoted reactions are specific acid or base processes). Some anions can effect displacement of leaving groups more rapidly than water (k_N) and in doing so catalyze hydrolysis via the sequence

$$RX + A^- \longrightarrow RA + X^-$$

$$RA + H_2O \rightharpoonup ROH + HA$$

$$(HA + X^- \rightleftarrows A^- + HX)$$

The use of nucleophilic anions such as phosphate or acetate at 1.0 M to 0.01 M to buffer hydrolysis reactions in the pH range 5-9 is a common and useful practice. The general acid- or base-catalyzed term $k_G[A^{\ddagger}]$ added to eq (2.15) to give

$$k_h = k_B[OH^-] + k_A[H^+] + k_N + k_G[A^{\ddagger}] \tag{2.25}$$

can often be as large as the specific acid or base terms because both $[H^+]$ and $[OH^-]$ are relatively low in the buffered region. As a result, the value of k_h may increase significantly in the presence of buffer salts. Table 2.2 lists values for k_G relative to k_N for specific ions in displacement reactions. However, the fact that primary and secondary salt effects also may be important makes it difficult to predict the overall direction or magnitude of such rate changes.

TABLE 2.2. NUCLEOPHILICITY CONSTANTS (n) FOR DISPLACEMENT REACTIONS

Anion	n^a
Cl^-	3.04
SO_4^{2-}	2.5
NO_3	1.03
HCO_3^-	3.8
HPO_4^{2-}	3.8
OAc^-	2.72
H_2O	0.00

[a] From the Swain-Scott relation $\log(k_G/k_N) = ns$, where s is a substrate-dependent constant that varied from 0.75 to 1.5; s for MeBr is 1.00 (Swain and Scott, 1953) k_G and k_N refer to specific rate constants for anion and water, respectively.

Effect of Solvent Composition

Chemists have commonly used mixed organic and water solvents to obtain concentrations of organic chemicals that make laboratory work convenient. Methanol, ethanol, dioxane, dimethyl sulfoxide, and acetone have been often used as cosolvents with water. While extrapolation of rate data from mixed solvents to pure water can be accomplished with moderate success for some hydrolytic reactions by use of empirical relationships such as the Winstein-Grunwald equation, the extrapolation contributes additional uncertainty. Additionally, the meaning of pH in such mixed solvent systems becomes questionable and requires what amounts to a double extrapolation to conditions of pH in pure water.

The effect of solvent composition is most pronounced in those reactions in which charge separation is well developed in the transition state, as, for example, in solvolysis of t-butyl chloride. In ethanol-water mixtures this hydrolysis is purely solvolytic--that is, no effect of acid or base is noted. Table 2.3 summarizes values of k_N, which increases by a factor of nearly 10^4 on going from 90% ethanol to water.

TABLE 2.3. EFFECT OF SOLVENT COMPOSITION ON THE RATE OF HYDROLYSIS OF t-BuCl IN ETHANOL/WATER AT 25°C[a]

Percent ethanol	k_N, s^{-1}
90	1.71(-6)
70	9.14(-6)
50	4.03(-6)
40	1.26(-4)
0	1.0(-2)[b]

[a] From Hughes (1935).
[b] Estimated from data in Table 4.1 of Mabey and Mill (1978).

Effects of Metal Ion Catalysis

A number of alkaline earth and heavy metal ions catalyze hydrolysis of a variety of organic esters (Bender, 1963; Martell, 1963). The principal function of the metal ion appears to be to increase the effective concentration of HO^- at pH levels where its concentration would otherwise be negligible (Martell, 1963; Buckingham and Engelhardt, 1975). This explanation is by no means universally applicable, especially to enzyme-like processes where prior complexation seems a necessary prelude to bond cleavage. Nonetheless, the kinetic features of several kinds of ester hydrolyses are similar, and they follow the same rate law

$$k_h = k_M K_A [M]_T / (K_A + [H^+]) + k_N + k_B \tag{2.26}$$

where k_h, k_N, and k_B have their usual significance, k_M is the metal ion catalysis constant, M is the total metal ion concentration, and K_A is the equilibrium constant for dissociation of the hydrated metal ion complex $M(H_2O)_x^{2+}$:

$$M(H_2O)_x^{2+} \rightleftharpoons M(H_2O)_{x-1}(OH)^+ + H^+$$

Kinetic analysis of several metal ion-catalyzed reactions indicates that at the concentrations of Cu or Mg ion found in aquatic or soil systems, the contribution of these reactions to the total rate of hydrolysis would be negligible.

2.7.3 General Environmental Considerations

Effects of Ion Concentration, Temperature, and pH

The preceding discussion shows that only ionic concentration, temperature, and pH will affect rates of hydrolysis in most natural waters. A review of water analyses for several hundred rivers indicates that the concentrations of inorganic salts in most aquatic environments are usually too low to have any effect of hydrolysis rates. Similarly, the concentrations of ions that can promote hydrolysis through catalytic mechanisms are generally so low that the catalyzed reaction rates will not compete with the specific acid- and base-promoted and neutral hydrolysis reaction rates. Furthermore, metal ions present in aquatic environments are probably complexed to natural organics and are not even available as catalysts at the low concentrations observed in water analyses.

Temperatures commonly encountered in aquatic systems range from freezing in some lakes during winter to 30°C in some ponds during summer. Since hydrolysis rates can vary by factors of 2 to 5 with each 10°C change, hydrolysis rates in the environment may vary seasonally by an order of magnitude. For compounds that do not show pH-dependent hydrolysis rates, temperature will be the major factor influencing their hydrolysis rates.

The pH values of natural waters can range from about pH 5 to 9, but they are usually close to 6.5 and result from several naturally occurring buffer systems. Eq 2.1 shows that for acid- or base-promoted reactions, a change of one pH unit will change the rate by an order of magnitude (at a maximum). Thus, for an ester hydrolysis (see Figure 2.4), the hydrolysis rate may increase by four orders of magnitude as the pH increases from 5 to 9.

Review of Literature on Hydrolysis in Natural Waters

A wealth of information has been published on the hydrolysis of a wide variety of organic compounds. However, most of the hydrolysis literature relating to environmental behavior concerns pesticides, particularly phosphorous esters. Much of this literature is incomplete for the range of either pH or temperature studied. Controls are seldom carried out (or at least reported) nor are precautions taken to eliminate adventitious processes such as volatilization or biodegradation. Effects of buffer salts and added organic solvents are often unrecognized.

Another problem with some reported studies is lack of data on effect of pH on the hydrolysis rate constant. Without such data, calculation of rate constants or half-lives at other pH values is not possible. In some studies the presence of buffer catalysis causes high hydrolysis rates, which introduces errors in the pH rate profile. When acid- and base-catalyzed processes are important, it may be difficult to determine whether a rate constant at an intermediate pH is due to a contribution from a neutral hydrolysis process or to buffer catalysis.

Few studies have been conducted that compare rates of hydrolysis of chemicals in buffered and in natural waters. This knowledge is critical to understanding hydrolysis in the environment. Results of some limited studies suggest that hydrolysis rates are the same in natural and buffered waters at the same pH and temperature; that is, naturally occurring organic and inorganic materials present in low concentrations in natural waters do not catalyze hydrolysis reactions.

Wolfe et al. (1977) studied the hydrolysis of methoxychlor in buffered waters and in two natural waters. Hydrolyses were carried out in buffered waters in the pH range 3 to 12 and at four temperatures between 45° and 85°C; below pH 8, the hydrolysis rate was found to be independent of pH. Rate constants at 27°C were calculated by extrapolation of these data. Hydrolysis reactions were carried out at 85°C in waters from the Oconee River (Athens, Georgia), pH 6.6, and from the Alabama River (Birmingham, Alabama), pH 7.2. Wolfe and coworkers found that reactions in the buffered and natural waters obeyed first-order kinetics and that there was no detectable difference in the hydrolysis rates between the two types of waters. At 85°C and below pH 8, the first-order (neutral) hydrolysis rate constant was about 5.2×10^{-5} s^{-1}, corresponding to a half-life of about 3.7 hr.

Zepp et al. (1975) investigated the hydrolysis of 2,4-dichlorophenoxyacetic acid esters (2,4-D) in buffered waters and in water from the Withlacoochee River (pH 8.1). They report that the hydrolysis rate measured in this water agreed well with the rate calculated from data obtained from experiments in buffered waters. The pH rate profile calculated from this data is presented in Figure 2.4.

Wolfe et al. (1977a) measured the hydrolysis of malathion in buffered waters and in a natural water sample from the Withlacoochee River in southern Georgia (pH 8.2). The experimentally determined half-life in the river water was 22 hr, in good agreement with the half-life of 20 hr calculated from data obtained from experiments in the buffered waters.

Smith et al. (1977) investigated the hydrolysis of methyl parathion in buffered waters, in four natural waters, and in one distilled water solution containing 9.5 ppm humic acid. These data are summarized in Tables 2.4 and 2.5; the pH-rate profile is given in Figure 2.6. The good agreement among the data in solutions below pH 8, where the neutral hydrolysis is dominant, indicates that natural waters do not catalyze hydrolysis of methyl parathion. In the early phase of the study, which used waters containing 0.067 M phosphate buffers, there was evidence of buffer catalysis. Subsequent use of acetate, borate, and phosphate buffers at 0.01 M concentrations eliminated the effect of buffer catalysis.

Weber (1976) has studied the hydrolysis of parathion in seawater. Data for the hydrolysis at 70°C in solutions that contain less than 10 ppm parathion are given in Table 2.6. Although it is difficult to reconcile the data with all the experimental variables in each experiment, by analogy to methyl parathion the half-life should be independent of pH up to about pH 8. From the data in Table 2.6, it appears that the rate of parathion hydrolysis is increased by increasing the ionic strength of the solution. Also, by

TABLE 2.4. FIRST-ORDER RATE CONSTANTS k_h FOR HYDROLYSIS OF METHYL PARATHION[a] AS A FUNCTION OF pH

pH	$k_h \times 10^7$ (sec^{-1})
3.00	6.80 (± 0.26)[b]
5.00	6.45 (± 0.33)
6.00	8.08 (± 0.52)
7.00	7.44 (± 0.24)
8.00	9.27 (± 0.17)
9.00	16.37 (± 1.39)
10.00	67.70 (± 1.1)
11.25	747 (± 166)

[a] Experiments used 26 μg ml^{-1} (1.0×10^{-4} M) methyl parathion at 40°C. Solvent was 1% acetonitrile in buffered distilled water.

TABLE 2.5. FIRST-ORDER RATE CONSTANTS k_h FOR HYDROLYSIS OF METHYL PARATHION IN NATURAL WATERS[a]

Natural water source	pH	$k_h \times 10^7$ (sec^{-1})
Lake Tahoe	7.6	12.41 (± 1.44)[b,c]
Lake Tahoe	7.6	6.31 (± 0.36)
Coyote Creek	7.8	7.54 (± 0.21)
Distilled water with 9.5 ppm humic acid[d]	5.25	5.99 (± 9.53)[d]
Aucilla River	6.07	6.10 (± 0.81)
Searsville Pond	7.5	6.83 (± 0.08)

[a] Except where noted, experiments used 26 μg ml^{-1} (1.0×10^{-4} M) methyl parathion at 40°C. Solvent was 1% acetonitrile in filtered natural water.

[b] Standard deviation.

[c] 0.26 μg ml^{-1} methyl parathion was used.

[d] 2.60 μg ml^{-1} methyl parathion was used.

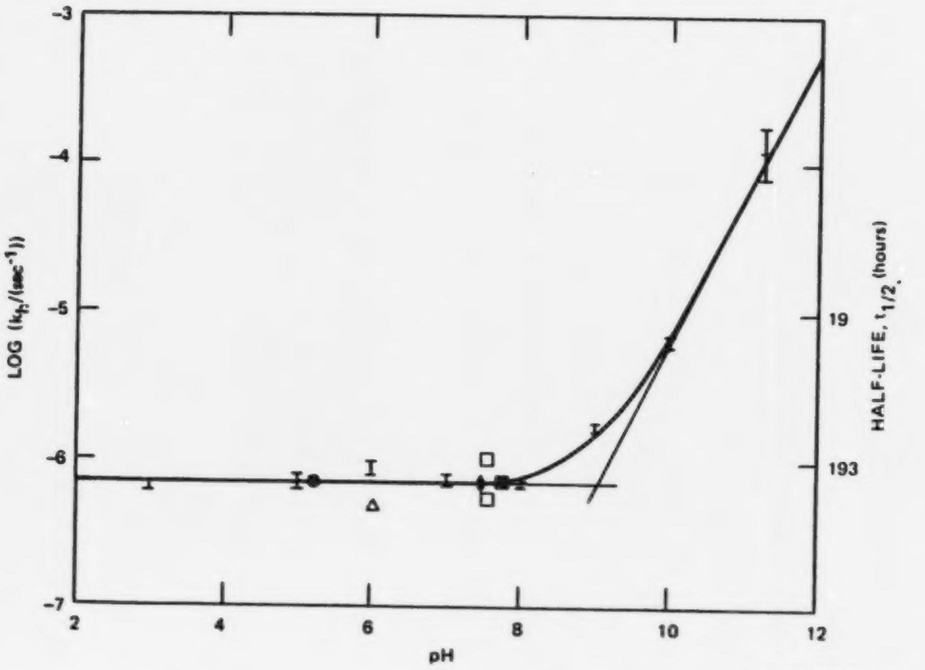

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Figure 2.6. PH Rate Profile for Methyl Parathion at 40°C. Points with bars: buffered distilled water (Table 2.4; see Smith et al., 1977) other points (Table 2.5), ● distilled H_2O with humic acid, Δ Aucilla River, ☐ Lake Tahoe, ♦ Searsville Pond, ■ Coyote Creek.

TABLE 2.6. HYDROLYSIS HALF-LIVES OF PARATHION IN VARIOUS AQUEOUS REACTION MEDIA AT 70°C.

Reaction media	pH	Half-life (hr)
Estuarine water, salinity 25.7 g l^{-1}	7.8	30.0 ± 0.9
Seawater, salinity 32.5 g l^{-1}	8.0	17.2 ± 0.3
Seawater + concentrated HCl	∿ 1	19.3 ± 0.5
Distilled water	5.9	39.2 ± 1.3
Distilled water + 30 g l^{-1} NaCl[a]	5.5	21.0 ± 0.7
Distilled water + dilute NaOH	8.6	22.7 ± 0.6
Buffer I,[b] total salt 30 g l^{-1}	7.9	15.7 ± 0.2
Buffer II,[c] total salt 0.6 g l^{-1}	7.5	31.8 ± 0.7

[a] 0.514 M NaCl, ionic strength = 0.5.

[b] Contains 0.063 M Na_2HPO_4, 0.003 M KH_2PO_4, and 0.313 M NaCl, ionic strength = 0.5.

[c] Contains 0.002 M Na_2HPO_4 and 0.001 M KH_2PO_4, ionic strength = 0.007.

TABLE 2.7. HYDROLYSIS OF ZECTRAN IN BUFFERED AND NATURAL WATER.

	Buffered waters			Natural waters[a]	
	pH 5.94	pH 7.00	pH 8.42	Solution A, pH 8.2	Solution B, pH 8.2 - 8.4
Temperature, 10°C					
$k_1 \times 10^3$ ($days^{-1}$)	6.6	9.2	20	12	12
$t_{1/2}$ ($days^{-1}$)	105.1	75.5	35.4	59.3	58.3
Temperature, 20°C					
$k_1 \times 10^3$ ($days^{-1}$)	15.0	27.0	160	76	110
$t_{1/2}$ ($days^{-1}$)	46.5	25.7	4.6	9.1	6.2
Temperature, 28°C					
$k_1 \times 10^3$ ($days^{-1}$)	19	100	550	470	540
$t_{1/2}$ ($days^{-1}$)	37.3	6.9	1.3	1.5	1.3

[a] See text for sources.

analogy to the previously discussed work on methyl parathion, some buffer catalysis effect may be present in the experiment in which the solution designated Buffer I was used (see Table 2.6). Although the effects operative in the hydrolysis of parathion in Weber's studies are complex, there appears to be no clear evidence that seawater possesses any particular catalytic effect other than ionic strength.

Matthews and Faust (1977) have reported the hydrolysis of Zectran, 4-dimethylamino-3,5-xylyl methyl carbamate, in buffered waters at pH values of 5.94, 7.00 and 8.42, and in water from the Musconctcong River, a stream in Central New Jersey (pH ∿ 8). The hydrolysis experiments were carried out at three temperatures--10°C, 20°C, and 28°C. Two solutions of the natural waters were prepared--one was filtered through a Millipore 0.45-μm filter (Solution B) and the second comprised half filter-sterilized water and half untreated river water (Solution A). The data are presented in Table 2.7.

From the data reported, it is impossible to construct a pH-rate profile in terms of a neutral and base-promoted hydrolysis. Moreover, since 0.05 M phosphate buffers were used, buffer catalysis is suspect. Because the hydrolysis rate constants were nearly the same in the unsterile and filter-sterilized water, biodegradation was not occurring. The slightly faster hydrolysis of 20°C in the sterile water compared to the unsterile water was noted and could not be explained by the authors; it is probably an experimental artifact.

If we assume that the hydrolysis rate at pH 8.42 in buffered water contained a minimal contribution from buffer catalysis, then the hydrolysis rate constants in the river water are in good agreement, which shows that no significant catalysis is occurring in the natural water.

The carbamate Sevin (N-methyl-1-naphthylcarbamate, also called Carbaryl) has also been the subject of hydrolysis studies, and of a controversy regarding the effect of natural waters on hydrolysis rates. Karinen et al. (1967) studied the hydrolysis of Sevin in seawater. In experiments carried out in the dark (Sevin is also light sensitive), in distilled water, in autoclaved seawater, and in filtered seawater similar degrees of transformation of Sevin were found after 4 days. All waters were adjusted to pH 7.8 with phosphate buffer. The authors reported only that the amount of Sevin hydrolyzed at 17°C, 20°C, and 28°C was 44%, 55%, and 93%, respectively. From the datum point at 20°C, we can calculate a half-life of 3.5 days.

A study on the hydrolysis of Sevin in 0.01 M phosphate buffers at 20°C over a pH range of 7 to 10 was conducted by Aly and El-Dib (1971), and they report a half-life of 1.3 days at pH 8. Citing a paper by Fukoto et al. (1967), which indicates that phosphate buffer does not affect hydrolysis rates of nitrophenyl carbamates, Aly and El-Dib concluded that the ionic strength of seawater was responsible for the slower rate of Sevin hydrolysis in seawater reported by Karinen.

A subsequent paper by Wauchope and Haque (1973) also reported the hydrolysis of Sevin in NaOH solutions at pH values of 9 - 10. These authors claim that the rate constants obtained in phosphate buffers by Aly and El Dib were too high, and concluded that there "... was little difference in carbaryl hydrolysis rate constants in NaOH solution versus seawater."

This apparent conflict in data shows several points commonly encountered in literature information, all of which arise from too few experiments or, at least, insufficient data that are reported. Assuming that the pH values of the studies of Karinen and Aly/El-Dib were actually 7.8 and 8.0, respectively, as reported, and that the reaction is a base-promoted process, then the first-order rate constant at pH 7.8 should be 0.63 of that at pH 8.0. Correcting the datum point of Karinen at pH 7.8 to 8.0 gives a half-life of 2.2 days, compared to 1.3 days reported by Aly and El Dib. This difference, less than a factor of two for measurements in two different laboratories, seems relatively small.

Neither Aly and El-Dib (1971) nor Wauchope and Hague (1973) attempted to repeat the same experiments reported by the previous investigator. All three papers neglect in some way to describe adequately the experimental procedures used and the data obtained. Therefore, it is not possible to make the comparisons necessary to resolve the discrepancies.

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Appendix 2.A*

A GENERAL SOLUTION FOR THE HYDROLYSIS REACTION RATE EQUATIONS

Using determinations of k_h at three values of pH(say pH = x, x + y and x + y + z), the first order reaction rates are obtained by solving the equations

$$
\begin{aligned}
k_h(x) &= 10^{-x}k_A + k_N + 10^{-14+x}k_B \\
k_h(x+y) &= 10^{-(x+y)}k_A + k_N + 10^{-14+(x+y)}k_B \qquad (2.A.1) \\
k_h(x+y+z) &= 10^{-(x+y+z)}k_A + k_N + 10^{-14+(x+y+z)}k_B
\end{aligned}
$$

for k_A, k_N, and k_B.

The solution of these equations is

$$
\begin{aligned}
k_A = \frac{1}{\beta}\Big\{&10^{x}(1-10^{-z})\,k_h(x) - 10^{x}(1-10^{-y-z})\,k_h(x+y) \\
&+ 10^{x-z}(1-10^{-y})k_h(x+y+z)\Big\} \qquad (2.A.2) \\
k_N = \frac{1}{\beta}\Big\{&-10^{-y}(1-10^{-2z})k_h(x) + (1-10^{-2y-2z})k_h(x+y) \\
&-10^{-z}(1-10^{-2y})k_h(x+y+z)\Big\} \\
k_B = \frac{1}{\beta}\Big\{&10^{14-x-2y-z}(1-10^{-z})k_h(x) - 10^{14-x-y-z}(1-10^{-y-z})k_h(x+y) \\
&+ 10^{14-x-y-z}(1-10^{-y})k_h(x+y+z)\Big\}
\end{aligned}
$$

where $\beta = 1 - 10^{-y} - 10^{-z} - 10^{-2y-2z} + 10^{-2y-z} + 10^{-y-2z}$

---

*This appendix was prepared by Francis W. Dresch of the Statistical Analysis and Computation Department.

If the lowest pH is 3 and the increments are at least 2--that is, if $x > 2$, $y \geq 2$, $z \geq 2$--$\beta \cong 1$ and other factors such as $1 - 10^{-y}$ are close to one. The solution can then be written more simply as

$$\begin{aligned} k_A &= 10^x k_h(x) - 10^x k_h(x + y) + 10^{x - z} k_h(x + y + z) \\ k_N &= -10^{-y} k_h(x) + k_h(x + y) - 10^{-z} k_h(x + y + z) \\ k_B &= 10^{14-x-2y-z} k_h(x) - 10^{14-x-y-z} k_h(x + y) + 10^{14-x-y-z} k_h(x+y+z) \end{aligned} \qquad (2.A.3)$$

For the recommended values of pH at 3, 7, 11 we have $x = 3$, $y = z = 4$ and these equations become those given in Section 2.6.3, equations 2.2 and 2.4. For this case, the variances are related by equations 2.8 through 2.10 given in Section 2.6.8.

In general, the coefficients in the variance equations are the squares of those in the equations for the relations among the k's. The coefficients in (2.A.3) must be squared to obtain relations among the variances. Thus we have in general

$$\begin{aligned} \sigma^2(k_A) &= 10^{2x}\, \sigma^2(x) + 10^{2x}\, \sigma^2(x+y) + 10^{2x-2z}\, \sigma^2(x+y+z) \\ \sigma^2(k_N) &= 10^{-2y}\, \sigma^2(x) + \sigma^2(x + y) + 10^{-2z}\, \sigma^2(x + y + z) \\ \sigma^2(k_B) &\approx 10^{28-2x-4y-2z}\, \sigma^2(x) + 10^{28-2x-2y-2z}\, \sigma^2(x+y) \\ &\quad + 10^{28-2x-2y-2z} \sigma^2(x+y+z) \\ &= 10^{28-2x-2y-2z} \left\{ 10^{-2y}\, \sigma^2(x) + \sigma^2(x+y) + \sigma^2(x+y+z) \right\} \end{aligned} \qquad (2.A.4)$$

where $\sigma^2(x) = \sigma^2[k_h(x)]$

$\sigma^2(x + y) = \sigma^2[k_h(x + y)]$

and $\sigma^2(x + y + z) = \sigma^2[k_h(x + y + z)]$.

Appendix 2.B*

TEMPERATURE EXTRAPOLATION

1. Extrapolation to Lower Temperatures

From the Arrhenius relation for either k_A, k_N, or k_B

$$k(T) = Ae^{-E/RT} = A(e^{-E/R})^{1/T} = A\rho^{1/T}$$

where $\rho = e^{-E/R}$. For two measured temperatures T_1 and T_2, we have

$$k(T_2)/k(T_1) = \rho^{1/T_2}/\rho^{1/T_1} = \rho^{1/T_2 - 1/T_1} = \rho^{(T_1-T_2)/T_1T_2}$$

$$\text{or } \rho = [k(T_2)/k(T_1)]^{T_1T_2/(T_1-T_2)} \qquad (2.B.1)$$

If T_o is the extrapolation temperature and $T_o < T_1 < T_2$, we have

$$k(T_o)/k(T_1) = \rho^{1/T_o-1/T_1} = \rho^{(T_1-T_o)/T_oT_1}$$

$$= [k(T_2)/k(T_1)]^{T_1T_2(T_1-T_o)/T_oT_1(T_1-T_2)}$$

$$\text{or} \quad k(T_o) = k(T_1)\ [k(T_2)/k(T_1)]^{-T_2(T_1-T_o)/T_o(T_2-T_1)}$$

$$= k(T_1)[k(T_2)/k(T_1)]^{-\alpha}$$

where $\alpha = \dfrac{T_2(T_1-T_o)}{T_o(T_2-T_1)} > 0$. We thus have finally:

$$k(T_o) = [k(T_1)]^{1+\alpha}[k(T_2)]^{-\alpha} \qquad (2.B.2)$$

which is applicable to each of the rate constants k_A, k_N, k_B

2. Expected Value and Standard Error of Extrapolated Rate Constants

If errors in measurement of the logarithm of the concentrations are normally distributed with zero mean and constant standard error σ, the statistical errors in the estimates $\hat{k}_n$ of the rate constant also follow a normal distribution because these estimates are linear functions of the logs of the concentration. Moreover, the estimates $\hat{k}_A$, $\hat{k}_N$, and $\hat{k}_B$ are also normally distributed since these are each linear functions of the relevant $\hat{k}_n$'s for each measured temperature. However, the extrapolating formula (2.B.2) above does not lead to a normal distribution for $k(T_o)$ even though $k(T_1)$ and $k(T_2)$ are normally distributed. The expected values for $k(T_o)$ and $\sigma[k(T_o)]$ can be calculated from series expansions as follows:

---

*This appendix was prepared by Francis W. Dresch of the Statistical Analysis and Computation Department

$$E[k(T_o)] = E[k(T_1)^{1+\alpha}\, k(T_2)^{-\alpha}] = E[k(T_1)^{1+\alpha}]\; E\,[k(T_2)^{-\alpha}] \qquad (2.B.3)$$

because observations at T_1 are independent from those at T_2. Similarly

$$E[k(T_o)^2] = E[k(T_1)^{2\alpha+2}]\; E[k(T_2)^{-2\alpha}] \qquad (2.B.4)$$

and

$$\sigma^2[k(T_o)] = E[k(T_o)^2] - \{E[k(T_o)]\}^2$$

$$= E[k(T_1)^{2\alpha+2}]E[k(T_2)^{-2\alpha}] - \{E[k(T_1)^{1+\alpha}]\}^2\{E[k(T_2)^{-\alpha}]\}^2 \qquad (2.B.5)$$

The series expansion is needed to estimate the expected value of (in general not integer) powers of a normally distributed variable k [either $k(T_1)$ with exponents $1 + \alpha$ and $2\alpha + 2$ or $k(T_2)$ with negative exponents $-\alpha$ and -2α]. If k is normally distributed with mean μ and standard error σ, we are interested in

$$E(k^m) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} (\mu+\sigma x)^m e^{-\frac{1}{2}x^2}\, dx = \frac{\mu^m}{\sqrt{2\pi}}\int_{-\infty}^{\infty} (1 + \frac{\sigma}{\mu} x)^m e^{-\frac{1}{2}x^2} dx \qquad (2.B.6)$$

This could be evaluated in terms of moments of x if m is a positive integer by expansion of

$$(1 + \frac{\sigma}{\mu} x)^m$$

by the binomial theorem. For noninterger m or negative m the binomial expansion becomes an infinite series, which converges only for

$$\frac{\sigma}{\mu} x < 1$$

To employ the series expansion we must truncate the normal distribution symmetrically at a point L, cutting off the distribution for $x > L$ and $x < -L$. The values are then defined to be

$$E(k^m) = \frac{\mu^m}{\sqrt{2\pi}}\int_{-L}^{L}(1 + \frac{\sigma}{\mu} x)^m e^{-\frac{1}{2}x^2} dx \Big/ \frac{1}{\sqrt{2\pi}}\int_{-L}^{L} e^{-\frac{1}{2}x^2}\, dx \qquad (2.B.7)$$

where $\frac{\sigma}{\mu} L < 1$ or $\mu > \sigma L$. If $L = 2$, for example, we must exclude k's for which the $\hat{k} < 2\,\sigma(\hat{k})$. Under these conditions we have

$$E(k^m) = \mu^m[1 + m \frac{\sigma}{\mu} E(x) + \frac{m(m-1)}{2} (\frac{\sigma}{\mu})^2 E(x^2) + \ldots] \qquad (2.B.8)$$

where $$E(x^n) = \frac{1}{\sqrt{2\pi}}\int_{-L}^{L} x^n e^{-\frac{1}{2}x^2} dx \Big/ \frac{1}{\sqrt{2\pi}}\int_{-L}^{L} e^{-\frac{1}{2}x^2} dx \qquad (2.B.9)$$

Evidently $E(x^{2n+1}) = 0$ for $n = 0, 1, 2, \ldots$

Integration by parts for even n gives

$$E(x^{2n}) = (2n - 1) E(x^{2n-2}) - cL^{2n-1} \qquad (2.B.10)$$

where $$c = \sqrt{\frac{2}{n}}\, e^{-\frac{1}{2}L^2} \Big/ \frac{1}{\sqrt{2\pi}} \int_{-L}^{L} e^{-\frac{1}{2}x^2} dx \qquad (2.B.11)$$

Thus $$E(x^2) = E(0) - c\,L = 1 - c\,L \qquad (2.B.12)$$

$$E(x^4) = 3E(x^2) - c\,L^3 = 3 - c(L^3 + 3L) \qquad (2.B.13)$$

etc.

We thus have

$$E(k^m) = \mu^m[1 + \frac{m(m - 1)}{2} \left(\frac{\sigma}{\mu}\right)^2 (1 - c\,L) + \ldots] \qquad (2.B.14)$$

$$E(k^{-m}) = \mu^{-m} [1 + \frac{m(m + 1)}{2} \left(\frac{\sigma}{\mu}\right)^2 (1 - c\,L) + \ldots] \qquad (2.B.15)$$

$$E[k(T_o)] = k_1^{1 + \alpha} k_2^{-\alpha} \left[1 + \frac{\alpha\,(\alpha + 1)}{2}\left(\frac{\sigma_1}{\mu_1}\right)^2 (1 - c\,L) + \ldots\right] \left[1 + \frac{\alpha\,(\alpha + 1)}{2} \left(\frac{\sigma_2}{\mu_2}\right)^2 (1 - c\,L) + \ldots\right]$$

$$= k_1^{1 + \alpha} k_2^{-\alpha} \left\{1 + \frac{\alpha\,(\alpha + 1)}{2} (1 - c\,L)\left[\left(\frac{\sigma_1}{\mu_1}\right)^2 + \left(\frac{\sigma_2}{\mu_2}\right)^2\right] + \ldots\right\} \qquad (2.B.16)$$

and the bias in $\hat{k}(T_o)$ from use of equation (2.B.2) is of the order of

$$\frac{\alpha(\alpha + 1)}{2} (1 - c\,L)\left\{\left[\frac{\sigma[\hat{k}(T_1)]}{k(T_1)}\right]^2 + \left[\frac{\sigma[k(T_2)]}{k(T_2)}\right]^2\right\} k(T_o) \qquad (2.B.17)$$

Similarly by use of (2.B.3), (2.B.5), (2.B.14), and (2.B.15) we have

$$\left\{\frac{\sigma[\hat{k}(T_o)]}{\hat{K}(T_o)}\right\}^2 = (1 - c\,L)\left\{(\alpha + 1)^2\left[\frac{\sigma[\hat{k}(T_1)]}{\hat{k}(T_1)}\right]^2 + \alpha^2\left[\frac{\sigma[\hat{k}(T_2)]}{\hat{k}(T_2)}\right]^2\right\} + \dots \tag{2.B.18}$$

where terms involving $\left(\frac{\sigma}{\mu}\right)^{2n} = \left[\frac{\sigma(k)}{k}\right]^{2n}$ of order $2\,n > 2$

have been neglected. Note that for $L = 1.95996$ for which

$\frac{1}{\sqrt{2\pi}}\int_{-L}^{L} e^{-\frac{1}{2}x^2}\,dx = 0.95$, $c = 0.12304$ and $1 - c\,L = 0.75884$

For $L = 3.09023$ for which

$$\frac{1}{\sqrt{2\pi}}\int_{-L}^{L} e^{\frac{1}{2}x^2}\,dx = 0.998,$$

$c = 0.0067477$ and $1 - c\,L = 0.97915$.

Appendix 2.C

KINETIC ANALYSIS OF PARALLEL FIRST-ORDER REACTIONS*

For the reactions

$$A \xrightarrow{k_1} B$$
$$A \xrightarrow{k_2} C$$
$$A \xrightarrow{k_3} D$$

the loss of A and appearance of B, C, and D can be formulated as

$$d[A]/dt = (k_1 + k \;\; + k_3)[A] = k[A]$$
$$\ln[A_o/A_t] = kt$$
$$A_t = A_o e^{-kt}$$

However since

$$d[B]/dt = k_1[A]$$
$$d[B]/dt = k_1 A_o e^{-kt}$$

Then

$$[B]_t = (k_1[A_o]/k)(1-e^{-kt})$$

Similarly, for C and D

$$[C]_t = (k_2[A_o]/k)(1-e^{-kt})$$

and

---

*From Frost, A. A., and R. G. Pearson, Kinetics and Mechanism (John Wiley and Sons, New York, 1967) p. 148.

$$[D]_t = (k_3[A_o]/k)(1-e^{-kt})$$

$$[B]_t/[C]_t = k_1/k_2$$

$$[B]_t/[D]_t = k_1/k_3$$

Since all products vary exponentially with the same rate constant k, all products have the same half-life

$$t_{1/2} = \ln 2/k$$

despite having different rate constants.

The rate constants k_1, k_2 or k_3 may be evaluated from a plot of concentration of product against $1-e^{-kt}$ where k for loss of reactant is evaluated in the usual way. The slope of the straight line (for B) is $k_1[A_o]/k$.

CHAPTER 3. PHOTOLYSIS IN WATER

by

W. R. Mabey, T. Mill, and D. G. Hendry

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3. PHOTOLYSIS IN WATER

3.1 INTRODUCTION

The effects of sunlight on biological systems and in weathering of materials has long been recognized. The variations in sunlight with season, time of day, and latitude govern many aspects of human life and agriculture. One of the early applications of photochemistry was by the armies of Alexander the Great, who used the rate of fading of dyed rags exposed to sunlight to measure time. More recently the chemical literature has provided ample evidence that photolysis of chemicals does occur in the atmosphere to produce photochemical smog; photochemical processes are also important in soil and aquatic systems. These protocols are designed to determine the rates of photolysis of chemicals in aquatic environments.

3.2 SUMMARY

Screening and detailed test protocols for direct photolysis of chemicals have been prepared to enable an investigator to estimate the photolysis rate constants and half-lives for chemicals in pure water or shallow depths of clear natural waters. Only chemicals with half-lives of less than three months are considered for detailed studies.

The test protocols are based on an extensive body of experimental and theoretical literature on photolysis together with a detailed kinetic analysis of direct photolysis. The recommended test protocols meet the criteria of quantitation, accuracy, and applicability to experimental systems and are cost effective and simple to use for a wide range of chemical structures. The theory and experimental procedures described in the literature are reviewed for the direct photolysis protocol. Indirect photolysis processes are also discussed, but only a screening test for indirect photolysis is recommended. The processes involved in indirect photolyses need to be studied further before a detailed test for indirect photolyses can be recommended.

The screening tests for direct and indirect photolyses of chemicals and a direct photolysis of a reference chemical (actinometer) are performed in sunlight experiments. The detailed test requires laboratory studies to obtain the following data:

- Absorption coefficients, ε_λ: The protocol requires ε_λ data at specified wavelengths to determine the ability of the chemical to absorb light within small, specific intervals around these wavelengths.
- Reaction quantum yield, ϕ: The detailed protocol requires the measurement of the reaction quantum yield for the chemical in air-saturated,

pure water to measure the efficiency with which a photochemical process converts absorbed light into chemical reaction.

The rate of loss of a chemical is given by

$$-\frac{dC}{dt} = k_{pE}[C] = [\phi\Sigma\varepsilon_\lambda L_\lambda][C] \qquad (3.1)$$

where L_λ is a term proportional to the light intensity in the wavelength interval λ averaged over a 24-hour (calendar) day, and k_{pE} is the first-order photolysis rate constant in units of day^{-1}. Data for L_λ as a function of decadic latitude and four season dates are given in Tables 3.2-3.5, Section 3.6. The rate constants k_{pE} apply to shallow depths of water (less than 0.5 meter) with very low absorbances (< 0.02) in the solar spectral region 290 nm to 825 nm.

3.3 CONCLUSIONS

Present knowledge of the theory and experimental aspects of direct photolysis reactions provides a sound basis on which to propose protocols for evaluating photolysis in water. The recommended screening and detailed studies for direct photolysis reactions represent a balance between the economic need to minimize laboratory work and the scientific requirements for sufficient and accurate data. The direct photolysis screening test is used to identify chemicals that have photolysis half-lives of less than three months in pure water. The detailed protocol can be used to measure the data necessary to manually calculate rate constants and half-lives for photolysis in clear water at shallow depths. The data can also be used to calculate direct photolysis rate constants in other aquatic environments, using a computer program available from the EPA-Athens Environmental Research Laboratory.

A screening test is also recommended to determine the effect of other substances present in natural waters on the photolysis rate of the chemical.

3.4 RECOMMENDATIONS

The protocols should be tested for applicability to several chemicals of environmental concern. Sunlight actinometers for use in the screening protocols should be selected from candidate chemicals and then validated for several seasons and latitudes. Although some data are available for validating the detailed protocol, the protocol should be tested using chemicals with a wider range of structure and reactivity.

Research is needed to determine what effects substances present in natural waters may have on photolysis rates, with an emphasis on the role of various sensitized and photo-initiated free radical processes in accelerating photolyses. Research is also needed on the effect natural substances may have on quenching or retarding photochemical processes.

3.5 SCREENING TESTS

3.5.1 Purpose

This screening test protocol is intended to identify chemicals with photolysis half-lives of less than three months.

3.5.2 Procedure

Solutions of chemical and an actinometer should be prepared using sterile, air-saturated, pure water and Reagent Grade (or purer) chemicals. Reactions mixtures should be prepared with chemicals at concentrations at less than one-half their solubility in water and at concentrations such that, at any wavelengths above 290 nm, the absorbance is less than 0.02 in the photolysis cell. If the chemicals are too insoluble in pure water to permit reasonable handling or analytical procedures, 1-volume % acetonitrile may be added to water as a cosolvent.

A solution of chemical should also be prepared in a natural water that has a measurable absorbance in the solar spectrum region above 290 nm. The natural water sample should be freshly collected (within 5 days of the photolysis experiment) and refrigerated until use. The natural water should be sterilized by filtration through a 0.22-μm filter; filtration also provides a reaction solution that is free of particulate so that reaction kinetics can be conducted in a homogeneous solution.

Solutions of chemicals and actinometer in sealed ampoules or stoppered flasks (with no greased joints) should be placed outdoors in sunlight beginning in early morning; whenever possible, these tests should be made in clear weather. The location should be free of excessive reflections from walls and windows and without morning or afternoon shadows. The tubes should be placed at an angle of about 30° from vertical. The reaction tubes should be placed in a transparent housing thermostated to maintain a constant temperature (± 2°C), preferably around 25°C. If possible, sunlight experiments should be done in summer to take advantage of longer sunlight periods and warm weather, in which case a housing is unnecessary.

Solutions should be analyzed for concentration of the chemical after 6 hours, 2 days (48 hours), 10 days (240 hours), and 4 weeks (672 hours). Whenever possible, an analytical procedure should be used that provides a precision within ± 5%. Solutions of the chemical and a standard should be maintained in the dark and analyzed at the above reaction times as controls on the sunlight experiments. Once 80% loss of the chemical is found, additional analyses of the chemicals are not necessary; the standard should be taken to two half-lives reaction time (i.e., 25% remaining standard).

3.5.3 Criteria for Screening Tests

If no loss of chemical or actinometer is found in the dark control solutions, any loss of chemical in the solutions in sunlight is assumed to be due to direct photolysis. Any loss of chemical or actinometer in the dark control solutions may indicate the intervention of some other loss process, and the possible importance of other transport or transformation processes should be checked before concluding that photolytic processes are occurring.

If the control solution data are satisfactory, the loss of chemical and actinometer should be interpreted in the following manner: If less than 20% of the chemical is lost after exposure to sunlight for four weeks, the chemical will have a photolysis half-life in water of over three months under all environmental sunlight conditions. If more than 20% is lost within 4 weeks, the data for 20% to 80% conversions may be used to calculate photolysis half-lives, $t_{1/2}$, as follows:

$$t_{1/2} = \frac{t_r(\ln 2)}{(\ln 1/X_r)} \qquad (3.2)$$

where X_r is the fraction of initial concentration remaining at time t_r. The experimental half-life for the chemical is designated $t_{1/2}^{ce}$.

The half-lives determined in this protocol are relevant to the day midway between the beginning and termination of the photolysis experiment and, therefore, represent an "average" half-life for the chemical during a certain time period. Obviously, the longer the experiment, the greater the change in half-lives during the experimental time period. Therefore, all photolysis half-lives that are reported should carry appropriate information on the duration of the experiment.

Since sunlight photolysis half-lives will vary with the time of year and day and with weather conditions, the experimental half-life for the chemical must be adjusted to a reference time of year, which is chosen to be the "winter date" (see Section 3.6.4). To do this, the measured photolysis half-life of the actinometer should be calculated according to equation (3.2) and is designated $t_{1/2}^{se}$. The half-life expected for the actinometer at the same midexperiment date should be determined from Figure 3.1 at the decadic latitude nearest the location of the experiment and is designated $t_{1/2}^{sc}$; the half-life for the actinometer at winter date is also determined from a figure such as Figure 3.1 and is designated $t_{1/2}^{scw}$. The half-life for the chemical in winter, $t_{1/2}^{cw}$, may then be estimated by equation (3.3):

$$t_{1/2}^{cw} = \frac{t_{1/2}^{sc}}{t_{1/2}^{se}} \; \frac{t_{1/2}^{scw}}{t_{1/2}^{se}} \left(t_{1/2}^{ce}\right) \qquad (3.3)$$

If $t_{1/2}^{cw}$ is less than one day, the chemical is considered to be nonpersistent and no further detailed studies are required. If $t_{1/2}^{cw}$ is greater than one day, but less than three months, detailed studies should be made to further define the rate parameters for photolysis of the chemical in sunlight. For

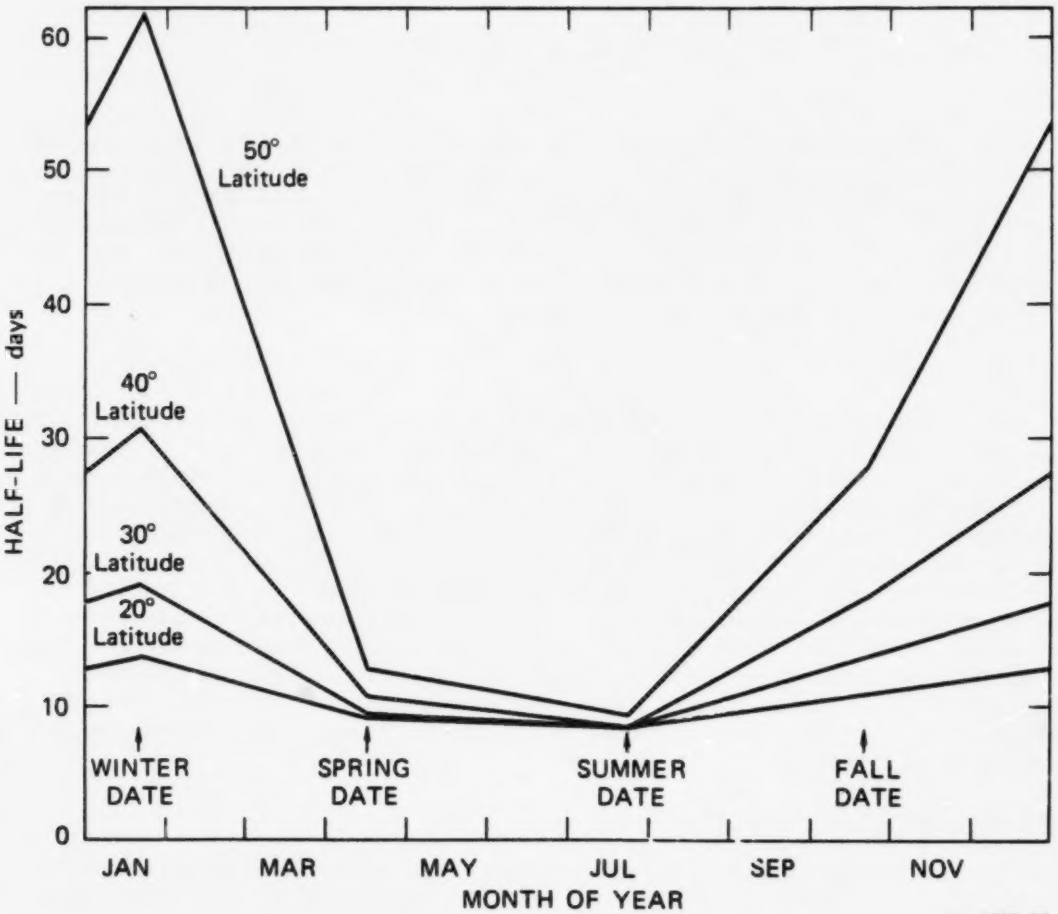

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FIGURE 3.1 ANNUAL VARIATION OF PHOTOLYSIS HALF-LIFE OF METHYL PARATHION ACTINOMETER

This figure does not include half-lives at summer and winter solstices.

example, a measured half-life for a chemical at 40° latitude is 30 days in April (April 1 to 31), and in the parallel experiment the measured half-life of methyl parathion (the actinometer) was found to be 18 days. Figure 3.1 shows that the average half-life for methyl parathion should have been 11 days in April (April 15); the half-life for methyl parathion at the winter date (Figure 3.1) is 32 days. The half-life estimated for the chemical for the winter date is then estimated by

$$\frac{11}{18} \times \frac{32}{18} \times 30 = 33 \text{ days}$$

The half-life for photolysis of a chemical in the natural water should be calculated using equation (3.2) and the datum point from the experiment in natural water. This half-life, $t_{1/2}^{nw}$, should be compared with the half-life measured in pure water in sunlight, $t_{1/2}^{e}$, to determine whether the presence of natural materials in water either retard or accelerate the photolysis rate of the chemical. The use of this information in an environmental assessment is discussed in the detailed protocol (Section 3.6.2).

3.5.4 Rationale

The screening test described above is a simple procedure for quantitatively evaluating sunlight photolysis of a chemical at a specific time of year and latitude, with a less accurate but still useful calculation used to determine how the photolysis may vary with the time of year. The test requires common laboratory chemicals and equipment and a location where the experiments can be performed in sunlight with reasonable temperature control. Sunlight is used as the irradiating source because of its obvious relevance as well as its low cost in comparison to artificial light sources. Simultaneous photolyses of a chemical and a sunlight actinometer provide a means of evaluating the sunlight intensities incident on the samples during the reaction time. Simultaneous photolyses of a chemical in pure water and in natural water provide a direct comparison to determine the effect natural substances may have on the photolysis rate of the chemical.

3.5.5 Scope and Limitations

The screening test for direct photolysis in pure water is designed to separate chemicals into two groups: those with half-lives of less than three months for which detailed studies are recommended, and those with photolysis half-lives of more than three months. The test procedure is simple and inexpensive but does require that the chemical be dissolved in water to obtain valid photochemical kinetic data. Additionally, if the chemical ionizes or undergoes structural changes within the environmental pH region of 5 to 9, photochemical reactions should be performed in the pH regions where the different ionized species structures are present.

3.6 DETAILED TESTS

3.6.1 Purpose

The objective of this test protocol is to provide a uniform procedure for calculating the rate constant for photolysis based on laboratory measurements in a manner that will enable investigators to estimate sunlight photolysis rate constants (k_{pE}) at any decadic latitude and season date (for example, midwinter at 40° latitude). The rate constants k_{pE} apply to environmental conditions of shallow depths (less than 0.5 meter) of natural waters with very low absorbances (< 0.02) in the solar spectral wavelength region 296 to 825 nm.

3.6.2 Direct Photolysis Half-life from ε_λ, L_λ, and ϕ Data

The rate constant k_{pE}, in units of day^{-1}, for direct photolysis of chemical at a specific latitude and season date is calculated from equation (3.4)

$$k_{pE} = \phi \Sigma \varepsilon_\lambda L_\lambda \tag{3.4}$$

where ϕ is the reaction quantum yield, ε_λ is the extinction coefficient of the chemical at the wavelength λ, and L_λ is the term proportional to the sunlight intensity in the wavelength interval λ. Values of L_λ for solar radiation from 296 to 825 nm are given in Tables 3.1 through 3.4; ε_λ and ϕ are measured according to procedures described in Sections 3.6.3 and 3.6.5, respectively. The half-life, $t_{\frac{1}{2}E}$, for the direct photolysis of the chemical at a specific date and latitude, which is determined by the L_λ data used in equation (3.4), is calculated by equation (3.5)

$$t_{\frac{1}{2}} = \ln 2 (k_{pE})^{-1} = \ln 2 / \phi \Sigma \varepsilon_\lambda L_\lambda \tag{3.5}$$

The calculation of the rate constant k_{pE} using equation (3.4) is performed by:

(1) Calculating the product of ε_λ and L_λ for each wavelength interval where ε_λ has a measurable value.

(2) Summing the products of $\varepsilon_\lambda L_\lambda$ over all wavelength intervals; the sum is equal to k_{aE}, which is a rate constant proportional to the absorption of light by chemical for the specific latitude and date and corresponds to the set of L_λ data used (k_{aE} in units of day^{-1}).

(3) Multiplying $\Sigma \varepsilon_\lambda L_\lambda$ by the reaction quantum yield, ϕ to obtain k_{pE}. In units of day^{-1}, k_{pE} corresponds to the photolysis rate constant that would be measured on a clear day for the chemical in dilute solution of clear water at very shallow depths (< 0.5 meter).

The range of photolysis rate constants that will be found in the continental United States can be found by calculating the rate constants and half-lives for winter date at 50°C latitude and summer date at 20° latitude, by

TABLE 3.1. L_λ VALUES FOR LATITUDE 20°N‡

λ Center	Spring	Summer	Fall	Winter
299	3.51(-4)	4.44(-4)	2.74(-4)	1.47(-4)
304	2.51(-3)	3.15(-3)	2.20(-3)	1.47(-3)
309	8.09(-3)	9.61(-3)	6.89(-3)	5.34(-3)
314	1.81(-2)	1.97(-2)	1.48(-2)	1.15(-2)
319	2.82(-2)	3.02(-2)	2.33(-2)	1.88(-2)
323	2.83(-2)	3.03(-2)	2.33(-2)	1.88(-2)
340	3.29(-1)	3.47(-1)	2.68(-1)	2.21(-1)
370	4.24(-1)	4.47(-1)	3.45(-1)	2.86(-1)
406	8.41(-1)	8.83(-1)	6.96(-1)	5.97(-1)
430	1.17	1.23	9.80(-1)	8.40(-1)
460	1.47	1.55	1.24	1.06
494	1.88	1.98	1.58	1.36
537	2.68	2.81	2.30	1.95
588	2.80	2.96	2.35	2.03
638	2.80	2.90	2.42	2.07
691	3.15	3.38	2.70	2.36
747	3.10	3.15	2.47	2.65
800	2.50	2.70	2.26	1.60

‡Units of L_λ are 10^{-3} einsteins cm^{-2} day^{-1}. Multiplication of L_λ by ε_λ in units of M^{-1} cm^{-1} gives rate constant in units of day^{-1}.

TABLE 3.2. L_λ VALUES FOR LATITUDE 30°N

λ Center	Spring	Summer	Fall	Winter
299	2.30(-4)	3.65(-4)	1.35(-4)	4.10(-5)
304	2.13(-3)	2.32(-3)	1.44(-3)	6.50(-4)
309	7.26(-3)	9.02(-3)	4.84(-3)	2.76(-3)
314	1.65(-2)	1.92(-2)	1.16(-2)	7.55(-3)
319	2.64(-2)	3.02(-2)	1.89(-2)	1.31(-2)
323	2.69(-2)	3.04(-2)	2.30(-2)	1.34(-2)
340	3.20(-1)	3.74(-1)	2.23(-1)	1.70(-1)
370	4.14(-1)	4.37(-1)	2.84(-1)	2.19(-1)
400	8.27(-1)	9.07(-1)	6.23(-1)	4.75(-1)
430	1.15	1.34	8.50(-1)	6.69(-1)
460	1.45	1.59	1.09	8.50(-1)
494	1.85	2.03	1.39	1.10
537	2.64	2.89	2.00	1.57
588	2.74	3.03	2.07	1.63
638	2.76	3.00	2.09	1.67
691	3.15	3.38	2.36	1.95
747	3.04	3.26	2.36	1.83
800	2.50	2.80	1.90	1.60

TABLE 3.3. L_λ VALUES FOR LATITUDE 40°N

λ Center	Spring	Summer	Fall	Winter
299	1.09(-4)	2.49(-4)	1.09(-4)	5.38(-6)
304	1.37(-3)	2.32(-3)	1.37(-3)	1.56(-4)
309	2.96(-3)	7.93(-3)	5.35(-3)	1.02(-3)
314	7.99(-3)	1.81(-2)	1.38(-2)	3.79(-3)
319	1.38(-2)	2.91(-2)	2.31(-2)	7.53(-3)
323	1.42(-2)	2.97(-2)	2.39(-2)	8.10(-3)
340	1.78(-1)	3.54(-1)	1.08(-1)	7.52(-2)
370	2.30(-1)	4.58(-1)	3.84(-1)	1.47(-1)
400	5.26(-1)	9.71(-1)	7.91(-1)	3.38(-1)
430	6.76(-1)	1.28	1.11	4.80(-1)
460	8.90(-1)	1.43	1.39	6.10(-1)
494	1.15	2.04	1.78	7.75(-1)
537	1.69	2.92	2.52	1.12
588	1.73	3.05	2.62	1.16
638	1.78	3.00	2.60	1.19
691	1.69	3.49	5.29	1.56
747	1.91	3.26	2.92	1.35
800	1.60	2.90	2.50	1.16

TABLE 3.4. L_λ VALUES FOR LATITUDE 50°N

λ Center	Spring	Summer	Fall	Winter
299	3.71(-5)	7.88(-6)	1.52(-4)	4.00(-7)
304	7.10(-4)	1.75(-3)	2.25(-4)	1.57(-5)
309	3.55(-3)	6.53(-3)	1.29(-3)	1.78(-4)
314	7.30(-3)	1.63(-2)	4.39(-3)	1.20(-3)
319	1.84(-2)	2.67(-2)	8.64(-3)	2.93(-3)
323	1.96(-2)	2.77(-2)	9.20(-3)	3.68(-3)
340	2.66(-1)	3.43(-1)	1.24(-1)	6.29(-2)
370	3.48(-1)	4.44(-1)	1.66(-1)	8.21(-2)
400	7.24(-1)	9.04(-1)	3.65(-1)	1.96(-1)
430	1.02	1.26	5.17(-1)	2.75(-1)
460	1.29	1.60	6.60(-1)	3.51(-1)
494	1.65	2.04	8.50(-1)	4.44(-1)
537	2.34	2.90	1.22	6.30(-1)
588	2.40	3.04	1.25	6.40(-1)
638	2.44	3.00	1.31	6.90(-1)
691	2.82	3.49	1.51	7.99(-1)
747	2.81	3.26	1.47	7.98(-1)
800	2.30	2.90	1.24	6.90(-1)

combining L_λ values in Tables 3.4 and 3.1, respectively, with measured ϕ and ϵ_λ values using equation (3.4).

By choice of the appropriate L_λ data, direct photolysis rate constants and half-lives may also be calculated for other latitude and date specific conditions. Although even more site and time specific data could be generated by interpolation between the decadic latitudes and four season dates for which L_λ data are given in Tables 3.1-3.4, such calculations do not seem warranted in view of the assumptions already included in the L_λ data presented and the ambient variations that influence the actual photolyses in aquatic environments. For most environmental assessments, the L_λ data for the decadic latitude and season date nearest the site and time of interest will be adequate (Variations in photolysis rates with latitude and date are discussed in Section 3.7.8.)

The rate constants k_{pE} and the half-lives calculated using the above procedure should be used in environmental assessments in conjunction with the half-lives measured in the screening tests for chemical in the pure and natural water in the following way: If the rate constants calculated and measured in pure water do not agree to within 50% of each other, further studies may be necessary to resolve the discrepancy. Possible sources of this discrepancy may be quantum yield is not constant over the entire wavelength region, the absorption of chemical has not been accurately or completely included in the calculation or adventitious loss processes such as volatilization may also have been occurring during the experiments and were not detected by the control experiments.

If the rate constants calculated and measured for the pure water solutions of a chemical agree within ± 50%, the pure water rate constants k_{pE} should be compared with the screening test experiment data for the natural water. If the rate constant in the natural water is more rapid than the rate constant for pure water, the pure water photolysis rate constant may be taken as the minimum photolysis rate in a natural water (i.e., photoreactions in natural waters may be faster than in pure water due to photosensitized or photoinitiated free radical reactions). If the rate constant in the natural water is slower than in pure water, then the pure water rate constant should be used in an environmental assessment with the warning that the photolysis rate in natural waters may be slower; an appropriate rate constant may be taken as the screening test photolysis rate constant measured in the natural water.

3.6.3 Measurement of the Absorption Coefficients, ϵ_λ

The absorption coefficients of the chemical should be determined for the wavelengths listed in the first column of Table 3.5. If the chemical is too insoluble in pure water for a reliable absorbance measurement, either acetonitrile or methanol may be used as a cosolvent. The amount of cosolvent used should be the minimal amount required to achieve a concentration that allows an accurate measurement of absorption coefficients above 290 nm. Particular care should be used to measure the extinction coefficients in the absorption "tail" of the spectrum as well as in the more intense absorption regions, since tailing absorptions may contribute significantly to the overall light absorption by the chemical in the solar spectrum region. In some cases, cells of longer pathlengths can be used to measure absorbances of chemicals that absorb light weakly even in saturated solutions; such cells are

TABLE 3.5. WAVELENGTH CENTER AND INTERVALS FOR L_λ (in nm)

λ Center[1]	Interval Range		Δλ
	From	To	
299	296.3	301.3	5.0
304	301.3	306.3	5.0
309	306.3	311.3	5.0
314	311.3	316.3	5.0
319	316.3	321.3	5.0
323	321.3	325.0	8.8
340	325.0	355.0	30.1
370	355.0	385.0	30.0
400	385.0	415.0	30.0
430	415.0	445.0	30.0
460	445.0	475.0	30.0
494	475.0	512.5	37.5
537	512.5	562.5	50.0
588	562.5	612.5	50.0
638	612.5	662.5	50.0
691	662.5	718.8	56.3
747	718.8	775	56.3
800	775	825	50.0

[1] Rounded off to unit wavelength.

also useful in measuring the absorption tails of some chemicals. If the absorption curve within the interval around wavelength λ (see Table 3.5) is reasonably flat, ε_λ may be determined from the absorbance at λ. If a large change in absorbance occurs within the interval, an averaged absorbance should be used to calculate ε_λ. The table presenting the ε_λ should state the method by which the ε_λ data were obtained (i.e., "based on average of the two absorbances at boundary of interval").

The absorption coefficients ε_λ should be calculated from the Beer-Lambert law

$$\varepsilon_\lambda = A_\lambda/(\ell[C]) \tag{3.6}$$

where A_λ is the absorbance at wavelength λ, ℓ is the cell pathlength (in cm), and [C] is the chemical concentration (in M); the units of ε_λ are then M^{-1} cm^{-1}.

For compounds of very low solubility, precautions should be taken to ensure that a homogeneous solution is used for absorbance measurements. Filtration of the chemical solution through a 0.22-μm filter or centrifugation to remove particulate are two ways to obtain homogeneous solutions. The absence of particulates can be verified by the failure of the solution to scatter a collimated beam of light.

When measuring absorption spectra for determining absorption coefficients, always run a solvent versus solvent spectrum to establish the baseline before measuring the spectrum of the chemical. At wavelengths where the absorbance is indistinguishable from baseline noise, the values of ε_λ should be entered as zero. In practice, the usual lower limit of absorbance measurement is about 0.01 absorbance unit (optical density); for a 10^{-2} M concentration of chemical in a 10-cm cell, this is equivalent to a measurable value of ε_λ of 0.1 M^{-1} cm^{-1}. When making such absorption measurements, use matched cells. When using long pathlength cells, make replicate measurements of absorbance and calculations of absorption coefficients to ensure that no instrumental or cell effects introduce artifacts into the absorption data.

3.6.4 L_λ Data

The L_λ data used in equation (3.1) (see Table 3.1-3.4) are proportional to the average light flux (in units of einsteins $liter^{-1}$ day^{-1}) that is available to cause photoreaction in the wavelength interval λ over a 24-hour day at a specific latitude and season date. The L_λ values were obtained using the computer program described by Zepp and Cline (1977), where the season date L_λ values were defined by the angle of declination of the sun at -20° for winter, -10° for fall, +10° for spring, and +20° for summer. The actual dates for a specific year that correspond to the angle of declination can be found in the American Ephemeris and Nautical Almanac. For the year 1978, the season dates for winter, spring, summer, and fall correspond to January 21, April 16, July 24, and October 20, respectively. The derivation of the L_λ data is discussed in Appendix 3.A. The L_λ values cover the solar spectral region from 296 nm to 825 nm in 18 wavelength intervals.

3.6.5 Measurement of Reaction Quantum Yield

The reaction quantum yield ϕ used in equation (3.1) should be measured by one of the three procedures described below. Procedures Q1 and Q2 require a merry-go-round photochemical reactor (MGRR) or a photochemical optical bench (POB) commonly used in laboratory photochemical studies. These two procedures usually provide rapid and reliable measurements of quantum yields with precision of ± 10%. Procedure Q3 requires photolysis experiments to be performed in sunlight, and the value of ϕ obtained by this method is subject to a potentially large, but as yet undetermined, error due to assumptions and the extended calculation required to calculate ϕ.

Photochemical Apparatus for Procedures Q1 and Q2

Several different designs of the photochemical apparatus for quantum yield measurements are possible, and the one used will depend on the equipment available and to some extent on the light source and filter systems chosen for the measurement. The apparatus used must have a light source, appropriate filters, sample holder and cells such that solutions of chemical and actinometer can be reproducibly irradiated with a uniform and constant amount of light limited to a discrete wavelength region and at a reasonably constant temperature (25 ± 2°C). If quantum yields are to be routinely measured, a section of the laboratory should be set aside and a permanent apparatus assembled using a merry-go-round reactor (MGRR) or an optical bench (POB). Two such possible apparatuses are discussed in Section 3.7.5.

The apparatus is designed so that the chemical is irradiated in a wavelength region where the chemical has an absorption coefficient that can be measured precisely. Experimental work is simpler if the wavelength region selected is one where the chemical has a large absorption coefficient. Often, however, the choices of wavelength regions will be determined largely by the light sources and light filter systems available or practical in a particular laboratory. Since some solution filter systems are more complex or less stable than others, and solutions are certainly more difficult to work with (but less expensive) than glass light filters, there is considerable latitude in setting up the photochemical apparatus. To avoid incurring a systematic error of between 10% to 50% due to temperature fluctuations, the temperature should be controlled to within ± 2°C in the reaction cell, and preferably around 25°C.

In addition to the information and discussion presented in Section 3.7.5, deMayo and Shizuko (1976), Murov (1973), and Calvert and Pitts (1966) have given excellent reviews and evaluations of equipment and components available for measuring quantum yields.

Procedure Q1: High Optical Density Actinometer

Procedure Q1, the preferred method for measuring ϕ, uses established actinometric procedures for measuring the light intensity flux entering a cell in a MGRR or a POB. Procedure Q1 is performed in two steps.

In Step 1, a solution of the actinometer chemical with a known quantum yield at the irradiating wavelength (ϕ_a) is prepared at an optical density greater than 2 and placed in a cell or cells on the MGRR or POB. The actinometer solution is photolyzed and analyzed to determine actinometer concentration, taking at least six time points. No data points should be taken after the optical density falls below 2.

The light intensity flux term, $I_{o\lambda}r$, entering the reaction cell can then be evaluated by either of two treatments:

(1) The concentration of the chemical, C , is plotted versus the time t, with the slope equal to a constant $k_z = \phi_a I_{o\lambda} r$, where C_t is the concentration of chemical at time t.

(2) A more accurate and precise value of k_z is obtained by a fit of the data by linear regression analysis to equation (3.7)

$$C_t = k_z t = [\phi_a I_{o\lambda} r]t \tag{3.7}$$

The zero-order rate constant k_z is in units of einsteins liter^{-1} sec^{-1} in photochemical light intensity and equal to M sec^{-1} in chemical concentration. The $I_{o\lambda}r$ term is then obtained from division of k_z by the known reaction quantum yield, ϕ_a, for the actinometer.

$$I_{o\lambda} r = k_z \phi_a^{-1} \tag{3.8}$$

In step 2, the reaction quantum yield ϕ is measured in an experiment in which a solution of chemical is photolyzed on the same MGRR or POB in a cell identical to that used in the actinometry to measure $I_{o\lambda}r$. The chemical concentration in water is adjusted to keep the absorbance in the irradiating wavelength region less than 0.02 a.u. The photolyzed reaction solution is analyzed for concentration of chemical at least six times between 10% and 80% reaction with one datum point after two half-lives (75% reaction).

The rate constant for direct photolysis at the wavelength interval can be evaluated by hand calculation or by calculator or computer:

(1) Plot the log of the concentration of chemical against time using semilog paper, with the best straight line through the points having a slope equal to $k_p/2.3$.

(2) Fit the data by linear regression analysis to the equation

$$\ln(C/C_o) = -k_p t,$$

where C and C_o are the concentrations of chemical at times t and 0, respectively.

The reaction quantum yield ϕ is then calculated from k_p using equation (3.9):

$$\phi = k_p[2.3I_{o\lambda}r\varepsilon_{\lambda c}\ell]^{-1} \qquad (3.9)$$

where $I_{o\lambda}r$ is the quantity measured above, $\varepsilon_{\lambda c}$ is the absorption coefficient of chemical at wavelength λ, and ℓ is the effective cell pathlength. The value of the effective cell pathlength must be either known or determined independently, since the quantity $I_{o\lambda}r$ measures the total light entering the solution and is independent of pathlength. A discussion of effective cell pathlength and its experimental determination is given in Section 3.7.5.

Procedure Q2: Low Optical Density Actinometer

Procedure Q2 is simpler than Q1 but suffers from the lack of actinometers that can be easily analyzed at low concentrations. Future development of appropriate dilute solution actinometers for use in Q2 offers promise for measuring reaction quantum yields rapidly and accurately.

Procedure Q2 is performed by preparing dilute aqueous solutions of an actinometer with a known quantum yield ϕ_a and chemical whose quantum yield is to be measured. The absorbance of both solutions should be less than 0.02 in the irradiating wavelength region. The solutions are photolyzed in identical cells in a MGRR or POB and analyzed for concentration of actinometer or chemical at reaction times between 10% and 80% loss of initial concentration for each species.

The rate constants k'_{pa} and k'_{pc} for direct photolysis of actinometer and chemical, respectively, can then be evaluated in two ways:

(1) Plot the log of the concentration of chemical against time using semilog paper, with the best straight line through the points having a slope equal to $k_p/2.3$.

(2) Fit the data by linear regression analysis to the equation

$$\ln(C/C_o) = -k_p t,$$

where C_t and C_o are the concentrations of chemical at times t and 0, respectively.

The quantum yield ϕ is then calculated from equation (3.10):

$$\phi = \left(\frac{k'_{pc}}{k'_{pa}}\right)\left(\frac{\varepsilon_{\lambda a}}{\varepsilon_{\lambda c}}\right)\phi_a \qquad (3.10)$$

where $\varepsilon_{\lambda a}$ and $\varepsilon_{\lambda c}$ are the absorption coefficients for actinometer and chemical, respectively, at the irradiating wavelength λ. Procedure Q2 is then simpler than Q1 in that it does not require measurement of the light intensity flux or knowledge of the effective pathlength of the reaction cell.

Procedure Q3: Sunlight Actinometer

Procedure Q3 requires photolysis rate constants k_{pE} for chemical and actinometer measured in sumultaneous experiments in sunlight. The same procedures and conditions used in the screening experiments apply in measuring rate constants in sunlight, except that at least five data points should be taken between 10% and 80% reaction of chemical and actinometer, with at least one point in each photolysis taken after two half-lives have occurred. Appropriate times for taking sample data points can be determined from the screening test data.

Data for loss of chemical during photolysis should be fit by regression analysis to the equation $\ln(C/C_o) = -k_p t$, where C and C_o are the chemical or actinometer concentrations at times t and 0, respectively. The increased number of data points provides a more precise rate constant k_{pE} than in the screening experiment and verifies that the photochemical reaction is first order in the chemical.

If the photolysis rate constant k_{pE} measured for the actinometer is within ± 50% of the value predicted from Figure 3.1 for the corresponding time of year and latitude, the reaction quantum yield ϕ for photolysis of chemical can be estimated as follows. From equation (3.1), the sunlight photolysis rate constants for chemical and actinometer are

$$k_{pcE} = \phi \Sigma L_\lambda \varepsilon_{\lambda c} \tag{3.11}$$

and

$$k_{paE} = \phi_a \Sigma L_\lambda \varepsilon_{\lambda a} \tag{3.12}$$

Since the photolyses were conducted simultaneously, L_λ values are the same. Subtracting and rearranging then gives

$$k_{pcE}\phi^{-1} = k_{paE}\phi_a^{-1} - \Sigma L_\lambda(\varepsilon_{\lambda c} - \varepsilon_{\lambda a}) \tag{3.13}$$

$$\phi = k_{pCE}[k_{paE}\phi_a^{-1} - \Sigma L_\lambda(\varepsilon_{\lambda c} - \varepsilon_{\lambda a})]^{-1} \tag{3.14}$$

where k_{pcE} and k_{paE} are the measured sunlight photolysis rate constants; $\varepsilon_{\lambda c}$ and $\varepsilon_{\lambda a}$ are the absorption coefficients at wavelength λ for chemical and actinometer, respectively; and ϕ_a is the known reaction quantum yield for the actinometer. L_λ data used in equation (3.13) should be chosen for the season date and latitude nearest the date and latitude where the sunlight experiments were performed.

3.6.6 Rationale

The foregoing detailed photolysis procedure is intended to provide accurate kinetic information concerning the photolysis rates of chemicals in shallow depths of clear water. The procedure requires close attention to control experiments and some temperature control in conducting the photolysis experiments. Data obtained from laboratory measurements of the reaction quantum yield and the absorption coefficients at specified wavelengths are then used with data from Tables 3.1 through 3.4 to calculate photolysis rate constants and half-lives at specific season dates and decadic latitudes.

3.6.7 Scope and Limitations

The foregoing detailed test protocol is intended to provide the quantitative information necessary to calculate rate constants for chemicals dissolved in water exposed to sunlight at four season dates and at the decadic latitudes of 20°, 30°, 40°, 50° within the continental United States. The rate constants calculated according to the procedure described above pertain to shallow depths of clear water. Information from the screening tests in pure and natural waters can then be used to determine whether photolyses in natural waters will be faster or slower than those estimated for the shallow, clear water conditions. The calculation of the sunlight photolysis rates constants and half-lives assumes a constant reaction quantum yield over the entire absorption spectrum of the chemical in the region 296 to 825 nm.

3.6.8 Error Analysis

Estimation methods for error analysis of the test protocol are based on certain assumptions concerning the accuracy of specific measurements and relationships between variables. The test protocols proposed here require measurements of concentrations of chemical as a function of time from which rate constants for photolysis are calculated using standard kinetic relationships. The discussion of error analysis follows the same sequence as the test protocol, beginning with measurement of k_z in the actinometer experiment through the calculation of the environmental photolysis rate constant k_{pE}:

$$k_z = C/t$$

$$I_{o\lambda}r = k_z/\phi$$

$$k_p = \ln(C/C_o)/t$$

$$\phi = k_p / 2.3\varepsilon_\lambda I_{o\lambda} r\ell$$

$$k_{pE} = \phi \Sigma \varepsilon_\lambda L_\lambda$$

Error Analysis for k_z

The estimate of the zero-order rate constant k_z measured in the actinometer experiment is related to the measured variables, concentration and time, by the following regression equation

$$k_z = \frac{n\Sigma tC - [\Sigma t][\Sigma C]}{n\Sigma t^2 - [\Sigma t]^2} \tag{3.15}$$

where C is concentration of chemical measured at time t. This version of the regression equation does not require that $(C/C_o) = 1$ at $t = 0$; that is, the line is not forced through the origin, and any significant departure from the origin indicates bias in values of C at $t > 0$.

The intercept C_o, the concentration at $t = 0$, is obtained from the equation

$$\ln(C_o) = \frac{1}{n}\Sigma C = k_z\left(\frac{1}{n}\Sigma t\right) \tag{3.16}$$

The preferred measure of error in experiments of this kind is the standard error, σ.* The standard error in k_h from n measurements is given by

$$\sigma(k_z) = \left(\frac{1}{n-2}\left[\frac{n\Sigma[C]^2 - [\Sigma C]^2}{n\Sigma t^2 - (\Sigma t)^2} - (k_z)^2\right]\right)^{\frac{1}{2}} \tag{3.17}$$

Equation (3.17) shows that σ varies approximately with $\frac{1}{\sqrt{n}}$ and directly with $\sigma(C)$.

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*The standard error may be expressed as the standard deviation, $(n \pm \sigma)$, the error ratio, σ/k, or percent error $(\sigma/k) \times 100$.

Error Analysis for $I_{o\lambda}r$

The equation used to calculate $I_{o\lambda}r$ is

$$I_{o\lambda}r = k_z\phi_a^{-1} \tag{3.18}$$

The standard error ratio is given by

$$\frac{\sigma(I_{o\lambda}r)}{(I_{o\lambda}r)} = \left[\frac{\sigma^2(\phi_a)}{(\phi_a)^2} + \frac{\sigma^2(k_z)}{(k_z)^2}\right]^{\frac{1}{2}} \tag{3.19}$$

For example, when the standard deviations in ϕ_a and k_z are both ± 5%, the error ratio is

$$\frac{\sigma(I_{o\lambda}r)}{(I_{o\lambda}r)} = [(0.05)^2 + (0.05)^2]^{\frac{1}{2}} = 0.071$$

or a percent standard deviation of ± 7.1% in $I_{o\lambda}r$.

Error Analysis for k_p

The estimate of the rate constant k_p is related to the measured variables, concentration and time, by the following regression equation.

$$k_p = \frac{n\Sigma t\ln C - [\Sigma t][\Sigma\ln C]}{n\Sigma t^2 - [\Sigma t]^2} \tag{3.20}$$

where C is concentration of chemical measured at time t. This version of the regression equation does not require that $\ln(C/C_o) = 0$ at $t = 0$; that is, the line is not forced through the origin and any significant departure from the origin indicates bias in values of C at $t > 0$.

The intercept, C_o, the concentration at $t = 0$, is obtained from the equation

$$\ln(C_o) = \frac{1}{n}\Sigma\ln C - k_p(\frac{1}{n}\Sigma t) \tag{3.21}$$

The preferred measure of error in experiments of this kind is the standard error, σ.* The standard error in k_p from n measurements is given by

$$\sigma = \frac{1}{n - 2}\left[\frac{n\Sigma[\ln C]^2 - [\Sigma \ln C]^2}{n\Sigma t^2 - (\Sigma t)^2} - (k_p)^2\right]^{\frac{1}{2}} \tag{3.22}$$

Equation (3.22) shows that σ varies approximately with $\frac{1}{\sqrt{n}}$ and directly with $\sigma(C)$.

Error Analysis for ϕ

The equation used to calculate the reaction quantum yield for photolysis of chemical is

$$\phi = k_p/2.3\varepsilon_\lambda I_{o\lambda} r \ell \tag{3.23}$$

where ε_λ and ℓ are defined in Section 3.6.5 and k_p and $I_{o\lambda}r$ are determined as above. The error ratio of ϕ is given by

$$\frac{\sigma(\phi)}{\phi} = \left[\frac{\sigma^2(k_p)}{(k_p)^2} + \frac{\sigma^2(\varepsilon_\lambda)}{(\varepsilon_\lambda)^2} + \frac{\sigma^2(I_{o\lambda}r)}{(I_{o\lambda}r)^2} + \frac{\sigma^2(\ell)}{(\ell)^2}\right]^{\frac{1}{2}} \tag{3.24}$$

For example, when the error ratios k_p, ℓ, ε_λ, and $I_{o\lambda}r$ are ± 0.05, 0.05, 0.04, and 0.07, respectively, the error ratio in ϕ is

$$\frac{\sigma(\phi)}{(\phi)} = [(0.05)^2 + (0.04)^2 + (0.07)^2 + (0.05)^2]^{\frac{1}{2}} = 0.108$$

or a percent standard deviation of ± 10.8% on ϕ.

Error Analysis for k_{pE}

The sunlight photolysis rate constant k_{pE} is calculated from

$$k_{pE} = \phi \Sigma \varepsilon_\lambda L_\lambda \tag{3.25}$$

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[*] The standard error may be expressed as the standard deviation form, $(k \pm \sigma)$, the error ratio, σ/k, or percent error $(\sigma/k) \times 100$.

The error ratio for k_{pE} is then

$$\frac{\sigma(k_{pE})}{(k_{pE})} = \left[\frac{\sigma^2(\phi)}{(\phi)^2} + \frac{\sigma^2 \Sigma \varepsilon_\lambda L_\lambda}{(\Sigma \varepsilon_\lambda L_\lambda)^2}\right]^{\frac{1}{2}}$$

$$= \left[\frac{\sigma^2(\phi)}{(\phi)^2} + \frac{\Sigma \sigma^2(\varepsilon_\lambda L_\lambda)}{(\Sigma \varepsilon_\lambda L_\lambda)^2}\right]^{\frac{1}{2}} \qquad (3.26)$$

where for each interval λ,

$$\frac{\sigma^2(\varepsilon_\lambda L_\lambda)}{(\varepsilon_\lambda L_\lambda)^2} = \left[\frac{\sigma^2(\varepsilon_\lambda)}{(\varepsilon_\lambda)^2} + \frac{\sigma^2(L_\lambda)}{(L_\lambda)^2}\right] \qquad (3.27)$$

The second term in equation (3.26) can be substituted by the terms in equation (3.27) where, if we assume the standard error ratio in ε_λ is ± 0.04 and in L_λ ± 0.10, then

$$\frac{\sigma^2(\varepsilon_\lambda L_\lambda)}{(\varepsilon_\lambda L_\lambda)^2} = [(0.04)^2 + (0.10)^2] = 0.0116$$

and

$$\sigma^2(\varepsilon_\lambda L_\lambda) = 0.0116(\varepsilon_\lambda L_\lambda)^2$$

Substitution of error ratios for ϕ and $\varepsilon_\lambda L_\lambda$ in equation (3.26) then gives

$$\frac{\sigma^2(k_{pE})}{k_{pE}^2} = 0.0116\left\{1 + \frac{\Sigma(\varepsilon_\lambda L_\lambda)^2}{(\Sigma \varepsilon_\lambda L_\lambda)^2}\right\}$$

Multiplication of the last term by ϕ^2/ϕ^2 and substitution of k_{pE}^2 for $\phi^2(\Sigma\varepsilon_\lambda L_\lambda)^2$ gives

$$\frac{\sigma(k_{pE})}{k_{pE}} = 0.108\left\{1 + \frac{\phi^2\Sigma(\epsilon_\lambda L_\lambda)^2}{k_{pE}}\right\}^{\frac{1}{2}} \geq 0.108$$

3.7 BACKGROUND

3.7.1 Definition of Photolysis

Photochemical transformation of chemicals can occur when energy in the form of light is absorbed by a molecule, placing it in an excited state from which reaction can occur. For these protocols we have chosen to define photochemical reactions as those processes that involve reaction of the excited state of the molecule of the chemical being evaluated for persistence.

Direct photolysis of chemicals occurs when the chemical molecule itself absorbs light and undergoes reaction from its excited state. Indirect photolysis occurs when another chemical species, called a sensitizer, absorbs light and the sensitizer transfers energy from its excited state to another chemical, which then undergoes reaction. This protocol includes photosensitized processes in a screening study, but not in a detailed study, since the quantitative details of photosensitized reactions in the environment are not yet established.

3.7.2 Kinetics of Photochemical Processes

There are many types of photochemical reactions, including oxidation, reduction, hydrolysis, substitution, and rearrangement. Molecules may undergo several of these reactions competitively depending on the structure and substitution of functional groups of the molecule as well as on the reaction conditions (such as, phase, solvent, other reactants, dissolved oxygen, wavelength of light, temperature). Since direct and sensitized photolyses may proceed through the same excited state of the molecule, the products of the photoreaction may often be the same. Several general references on photochemistry include Calvert and Pitts (1966), Turro (1967), Crosby (1972), and Murov (1973).

In practice it is possible to measure the rate constant for a photochemical reaction or a reaction quantum yield without knowing the type of reaction that is occurring. For environmental applications, data from measurements made under environmentally relevant conditions, such as air-saturated water, at or near 25°C, and at wavelengths above 290 nm, can be used to predict probable loss rates in sunlight without additional knowledge of the chemistry. However, some knowledge of the photochemistry, including the effects of oxygen, pH, and temperature and the products formed, are useful in planning detailed photochemical studies and in providing an overall fate assessment.

3.7.3 Kinetics in Solution

Light Absorption and Energy Relationships

The Beer-Lambert law for light absorption relates the incident light, I_o, on a solution of chemical, to the light emergent from the solution, I, according to equation

$$\log_{10}(I_o/I) = \varepsilon C \ell = \text{Absorbance} \tag{3.28}$$

where ε is an absorption constant characteristic of the light-absorbing chemical, C is the concentration of chemical in solution, and ℓ is the pathlength of the cell containing the solution. Equation (3.28) may also be rewritten in the exponential form

$$I = I_o 10^{-\varepsilon C \ell} \tag{3.29}$$

The amount of light absorbed, I_a, is then

$$I_a = I_o - I = I_o(1 - 10^{-\varepsilon C \ell}) \tag{3.30}$$

In this discussion, the absorption of light in a solution will be confined to a single narrow wavelength region λ; an additional term, α_λ, called the light attenuation coefficient will be used to account for unknown substances other than the chemical in solution that contribute to light absorption:

$$I_{a\lambda} = I_{o\lambda}[1 - 10^{-(\alpha_\lambda + \varepsilon C)\ell}] \tag{3.31}$$

The α_λ parameter is conveniently defined as a composite of the absorption constant and concentration(s) of the unknown substance(s) dissolved in water of 1 cm pathlength, and is in units of cm^{-1}.

The absorption of light by a chemical results in formation of an excited state of the molecule, with the energy (E) of the initial excited state determined by the wavelength λ of the absorbed light

$$E = h\nu = \frac{hc}{\lambda} \tag{3.32}$$

where E = energy (ergs)
h = Planks constant (6.62×10^{-27} erg-sec)
ν = frequency of light absorbed (cm^{-1})
c = velocity of light (3.00×10^{8} meter sec^{-1})
λ = wavelength of absorbed light (nm)

The unit of light on the molecular level is called a photon or quantum. In molar terms, equation (3.32) is then

$$E = Nh\nu = \frac{Nhc}{\lambda} \tag{3.33}$$

where N is Avogadro's number, 6.02×10^{23} molecules or quanta per mole. A mole of quanta is called an einstein. Some energies corresponding to wavelengths λ are given in Table 3.6.

In photochemical kinetics, the rate at which the photons are delivered to a reaction system directly determines the photolysis rate of a chemical. The most useful unit of light flux for kinetic equations are einsteins cm^{-2} sec^{-1} nm^{-1}. Specification of a light pathlength then allows the light flux to be expressed in volume units, einsteins $cm^{-3} sec^{-1}$ nm^{-1}, by simple division.

Units of einsteins cm^{-2} sec^{-1} nm^{-1} should be clearly contrasted to the energy units of watts cm^{-2} nm^{-1}, which are commonly reported in the literature for meterological data; the watt is defined as joule sec^{-1} and is wavelength dependent (see Table 3.6). The conversion of watts cm^{-2} nm^{-1} to einsteins cm^{-2} sec^{-1} nm^{-1} is given by equation (3.34).

$$I(\text{einsteins } cm^{-2}\ sec^{-1}\ nm^{-1}) = I(\text{watts } cm^{-2}\ nm^{-1}) \times \lambda \times 3.03 \times 10^{39} \tag{3.34}$$

Quantum Yield

The Grotthus-Draper law states that "only light absorbed by a molecule can bring about a photochemical change." The Stark-Einstein law modified this statement in accord with quantum theory to state that "a molecule which undergoes a photochemical change does so as the result of the absorption of a single quantum of energy." However, often less than one mole of chemical reacts for each einstein of light absorbed as a result of radiationless transitions, phosphorescence, or fluorescence. In a few cases each einstein of light absorbed results in reaction of more than one mole of chemical as a result of

TABLE 3.6. WAVELENGTH-ENERGY RELATIONSHIPS

Wavelength	λ, nm	kcal $mole^{-1}$ [a]	kJ $mole^{-1}$ [b]
Ultraviolet	200	143.0	598.5
	300	95.3	399.0
	350	81.7	341.8
Violet	400	71.5	299.3
Blue	450	63.6	266.1
Green	500	57.2	239.4
Orange	600	47.7	199.5
Red	800	35.8	149.8

[a] energy = $2.86 \times 10^4(\lambda^{-1})$ kcal $mole^{-1}$

[b] energy = $1.20 \times 10^5(\lambda^{-1})$ kJ $mole^{-1}$

chain reactions. A few rare cases are also known where a molecule absorbs two quanta before reaction (double photon reactions). Direct absorption of light is not required, however, if another light-absorbing molecule can transfer part of its excitation energy to effect a sensitized reaction.

This variable efficiency of the photochemical process has led to the definition of the efficiency of photochemical reactions expressed as a reaction quantum yield ϕ:

$$\phi = \frac{\text{Number of moles chemical reacted}}{\text{Number of einsteins absorbed}} \qquad (3.35)$$

Since the term quantum yield is also applied to other photochemical processes including fluorescence, phosphorescence, and sensitizations, the term "reaction quantum yield" should always be explicitly stated.

Rate Laws and Constants

Basic Photochemical Rate Equation: Knowledge of the light incident on a reaction system I_o, the absorption constant for a chemical undergoing reaction

ε_λ, and the quantum yield ϕ then provide the complete basis for expressing the kinetics of photochemical reactions.

The equation describing the rate of photolysis of a chemical in solution at wavelength λ is

$$-\frac{dC}{dt} = \phi I_{o\lambda}\left(\frac{A}{V}\right)F_{s\lambda}F_{c\lambda} \tag{3.36}$$

where A is the area (in cm²) exposed to the incident light intensity $I_{o\lambda}$ (in einsteins cm⁻² sec⁻¹) V is the volume of solution (in liters), $F_{s\lambda}$ is the fraction of light absorbed by the system, and $F_{c\lambda}$ is the fraction of absorbed light that is absorbed by the chemical in the system.

$$F_{s\lambda} = 1 - 10^{-(\alpha_\lambda + \varepsilon_\lambda C)\ell} \tag{3.37}$$

$$F_{c\lambda} = \frac{\varepsilon_\lambda C}{\alpha_\lambda + \varepsilon_\lambda C} \tag{3.38}$$

For a given reaction cell, the term (A/V) is a constant, which is designated r in this discussion.* Equations (3.36), (3.37), and (3.38) are combined to obtain:

$$-\frac{dC}{dt} = \phi I_{o\lambda}r[1 - 10^{-(\alpha_\lambda + \varepsilon_\lambda C)\ell}]\ \frac{\varepsilon_\lambda C}{\alpha_\lambda + \varepsilon_\lambda C} \tag{3.39}$$

For use in kinetic studies, the differential equation (3.39) requires integration into a form that expresses the concentration of chemical C as a function of time t . For the case when $\alpha_\lambda << \varepsilon_\lambda C$, equation (3.39) simplifies to

$$-\frac{dC}{dt} = \phi I_{o\lambda}r(1 - 10^{-\varepsilon_\lambda C\ell}) = a(1 - e^{-bC}) \tag{3.40}$$

---

*In practice, the terms A, V, and ℓ have useful measurable dimensions only for cells with planar windows; A and ℓ lose obvious dimensional relationships when round cells are used. This problem is discussed in Section 3.7.5.

where $a = \phi I_{o\lambda} r$
$b = 2.3\varepsilon_\lambda \ell$

Integration of equation (3.40) then gives equation (3.41), (see Appendix 3.B for details of this integration)

$$\frac{e^{bC}-1}{e^{bC_o}-1} = e^{-ab(t - t_o)} \tag{3.41}$$

where C and C_o are the concentrations of chemical at times t and t_o. When $t_o = 0$, equation (3.41) can be simplified further:

$$\frac{e^{bC}-1}{e^{bC_o}-1} = e^{-abt} \tag{3.42}$$

or

$$\ln\left[\frac{e^{bC}-1}{e^{bC_o}-1}\right] = - abt \tag{3.43}$$

A plot of $\ell n(e^{bC}-1)$ against t gives a straight line with a slope equal to -ab. Since a is equal to $\phi I_{o\lambda} r$ and b is known, either ϕ or the light intensity flux $I_{o\lambda} r$ may be calculated if the other quantity is known. Equation (3.40) may be further simplified if limiting conditions are chosen so that $\varepsilon_\lambda C\ell$ is either very small or very large. When $\varepsilon C\ell < 0.02$, the term $10^{-\varepsilon C\ell} \sim 2.3\varepsilon\ell[C]$ and the rate expression becomes first order

$$\begin{aligned} -\frac{dC}{dt} &= 2.3 I_{o\lambda} r \varepsilon_\lambda \ell \phi [C] \\ &= k_p [C] \end{aligned} \tag{3.44}$$

Integration of equation (3.44) gives the usual first-order expression

$$\ln([C]/[C_o]) = -k_p t \tag{3.45}$$

and a plot of $-\ln[C_t]$versus t gives k_p.

When the incident light is nearly completely absorbed by the solution, $\varepsilon[C]\ell > 2.0$, equation (3.40) again simplifies since $10^{-2.0} = 0.01$, $(1 - 0.01) \sim 1$, and equation (3.40) becomes

$$-\frac{dC}{dt} = \phi I_{o\lambda} r = k_z \qquad (3.46)$$

Integration of equation (3.46) gives the zero-order relation

$$C_o - C = k_z t \qquad (3.47)$$

Equation (3.47) is used commonly to evaluate the incident flux in a photochemical experiment where the standard chemical or actinometer absorbs all light incident on the cell during the course of the reaction. When k_z is measured in this way, then from equation (3.46)

$$I_{o\lambda} r = k_z \phi^{-1} \qquad (3.48)$$

where $I_{o\lambda}$ is in units of einsteins liter^{-1} sec^{-1}

Environmental Photolysis Rates: The rate of loss of a chemical in dilute solution in an environmental water body is given by equation (3.39), modified to account for the depth of the water body

$$-\frac{dC}{dt} = \phi \frac{I_{o\lambda}}{D}[1 - 10^{-(\alpha_\lambda + \varepsilon_\lambda C)\ell}]\left[\frac{\varepsilon_\lambda C}{\varepsilon_\lambda C + \alpha_\lambda}\right] \qquad (3.49)$$

where $D = 1/r$. We can use equation (3.49) to develop an expression for rate of loss of chemical in dilute solution in sunlight.

In shallow clear water where the total absorbance by both water and chemical is < 0.02, equation (3.49) simplifies to

$$-\frac{dC}{dt} = \phi \frac{I_{o\lambda}}{D} 2.3\ell(\alpha_\lambda + \varepsilon_\lambda C)\left[\frac{\varepsilon_\lambda C}{\varepsilon_\lambda C + \alpha_\lambda}\right] \qquad (3.50)$$

Since at very low concentrations in natural waters the chemical absorbs only a small fraction of the light ($\alpha_\lambda >> \varepsilon_\lambda C$), equation (3.49) further simplifies to

$$-\frac{dC}{dt} = \phi\frac{I_{o\lambda}}{D}2.3\ell\varepsilon_\lambda[C] \qquad (3.51)$$

This same result is obtained if $\alpha_\lambda << \varepsilon_\lambda C$. Equation (3.51) can be used to estimate the photolytic rate constant k_p under environmental conditions if appropriate data are available. The composite term $I_{o\lambda}\ \ell/D$ is related to the manner in which sunlight enters and passes through a water body; Zepp and Cline have analyzed the reflection and refraction of light at the water-air interface in terms of light intensity, light pathlength and vertical water depth for use in a computer calculation of environmental photolysis rates (see Appendix D). From their program, we have prepared a compilation of light intensity terms, $L_\lambda = 2.3\ I_{o\lambda}\ell/D$, for four seasonal dates at each specific decadic latitude at shallow water depths. The L_λ data are in units of einsteins-cm liter^{-1} day^{-1} to provide a smoothed rate constant that takes into account diurnal fluctuations in sunlight intensity. With substitution of L_λ, equation (3.51) then simplifies to

$$-\frac{dC}{dt} = \phi\varepsilon_\lambda L_\lambda[C] \qquad (3.52)$$

$$k_p = \phi\varepsilon_\lambda L_\lambda \qquad (3.53)$$

and

$$\ln([C]/[C_o]) = -k_p t \qquad (3.54)$$

where k_p is actually the product of a rate constant for light absorption and the quantum yield ($k_p = \phi k_a$).

Equations (3.52) and (3.53) refer to the rate of photolysis at one wavelength; to determine the total rate constant for photolysis in sunlight, k_{pE}, equation (3.54) may be used to evaluate k_{pE} from experiments in sunlight (Section 3.6.5) or equation (3.53) may be used to calculate k_{pE} by summing the terms for $\varepsilon_\lambda L_\lambda$ at each wavelength for which the product $\varepsilon_\lambda L_\lambda > 0$, assuming ϕ is constant over all wavelengths:

$$k_{pE} = \phi\Sigma\varepsilon_\lambda L_\lambda \qquad (3.55)$$

3.7.4 Effects of Environmental Variables

Temperature Effects

The effect of temperature on photochemical processes in solution has usually been considered minimal since reactions occurring from the electronic excited state were assumed to have little or no activation energies. However many photochemical reactions do have activation energies of 3 to 7 kcal mole^{-1} (Barltrop and Coyle, 1975). For a reaction with an energy of activation (E_a) of 5 kcal mole^{-1}, the rate constant will change by a factor of 2.5 going from 0°C to 30°C. Over the same temperature range, rate constants will vary by factors of 4 and 1.6 for $E_a = 7.5$ and 2.5 kcal mole^{-1}, respectively. Therefore, some reliable temperature control to ±2°C is necessary to achieve accurate measurement of photochemical rate constants and quantum yields, especially in outdoor screening experiments where large ambient temperature effects are common.

Solvent Effects

While extensive information is available regarding the effects of solvents on photochemical reactions, this discussion will be limited to water as the major solvent because of the obvious environmental application. Ordinarily, water is unreactive in free radical reactions and does not act as a sensitizer. Water does react in photonucleophilic reactions, sometimes called photohydrolysis reactions; the mechanistic details of these processes have not been established, and the reactions may be pH dependent (Crosby et al., 1972). Other studies have shown that photolyses of some polynuclear aromatic hydrocarbons are much faster in aqueous solutions than in organic solvents (Smith et al., 1978,) but the information available is not sufficient to determine the exact role of water in these reactions. In view of the differences between the reactivity of water and organic solvents, environmentally relevant experimental studies should be performed in water as the major (> 98%) solvent, and, if possible, the only solvent.

However, since the solubilities of most organic chemicals in water are low enough to be a major problem in practical laboratory studies, the choice of an appropriate cosolvent needs careful examination. Many organic solvents are themselves immiscible with water and are therefore obviously poor cosolvents. Soluble cosolvents such as some ethers and alcohols (i.e., dioxane, tetrahydrofuran, ethanol, methanol) are subject to radical hydrogen transfer reactions and would be unsuitable for some photochemical reactions. Other solvents, such as acetone, are photosensitizers and should be avoided. Our careful consideration of common and practical cosolvents indicates that only acetonitrile comes close to being an ideal cosolvent for use in photochemical studies and is the only cosolvent recommended in these protocols.

Light-Screening Effects of Natural Organics

The rates of photolysis of chemicals in aquatic environments will also be affected by the natural substances present in these waters. Some properties of light transmitted in natural waters have been discussed by Kirk (1977), Zepp and Cline (1977), and Hutchinson (1957). The substances present in natural waters may serve as light absorbers or as photochemical excited state quenchers or sensitizers.

In waters that have high optical densities owing to naturally occurring substances such as humic and fulvic acids, light may be absorbed and therefore not available to cause photoreaction of chemicals. To account for such a light-screening effect in natural waters, the computer program of Zepp and Cline (1977) has the capacity to include the α_λ term (equation 3.49) to account for the attenuation of light by natural substances in water. The kinetic data calculated using the program are then expressed as the average rate constant (or half-life) for a chemical for the specified depth of the water body. Obviously, the averaged photolysis rate will decrease with increasing depth of the water when the natural water absorbs appreciable light; of course, when the depth parameters are set to calculate near surface photolysis rate constants ($\alpha_\lambda \ell \simeq 0$), the rate constants for natural and pure water are the same.

The fractional reduction in photolysis rate constant in a natural water compared with a pure water over a wavelength interval can be determined in the following manner: for a very dilute solution of a chemical in pure water, the photolysis rate constant for the chemical is given by

$$k_p = 2.3\phi I_{o\lambda} r \varepsilon_\lambda \ell \qquad (3.56)$$

In a natural water where $\alpha_\lambda >> \varepsilon_\lambda C$, and from equation (3.39), the rate constant for the chemical in the natural water $k_{p\alpha}$ is

$$k_{p\alpha} = \phi I_{o\lambda} \frac{r\varepsilon_\lambda}{\alpha_\lambda}[1 - 10^{-\alpha_\lambda \ell}] \qquad (3.57)$$

Division of equation (3.57) by equation (3.56) then gives the ratio of rate constants, which is the light-screening factor S:

$$S = \frac{k_{p\alpha}}{k_p} = \frac{1 - 10^{-\alpha_\lambda \ell}}{2.3\alpha_\lambda \ell} \qquad (3.58)$$

Figure 3.2 shows how S varies with the quantity $\alpha_\lambda \ell$, where α_λ is the absorbance of the natural water in a 1-cm cell.

Chemical Effects of Natural Organics and Oxygen

Dissolved or suspended organics may accelerate or retard photolyses by chemical processes that assist, compete, or interfere with the direct reaction.

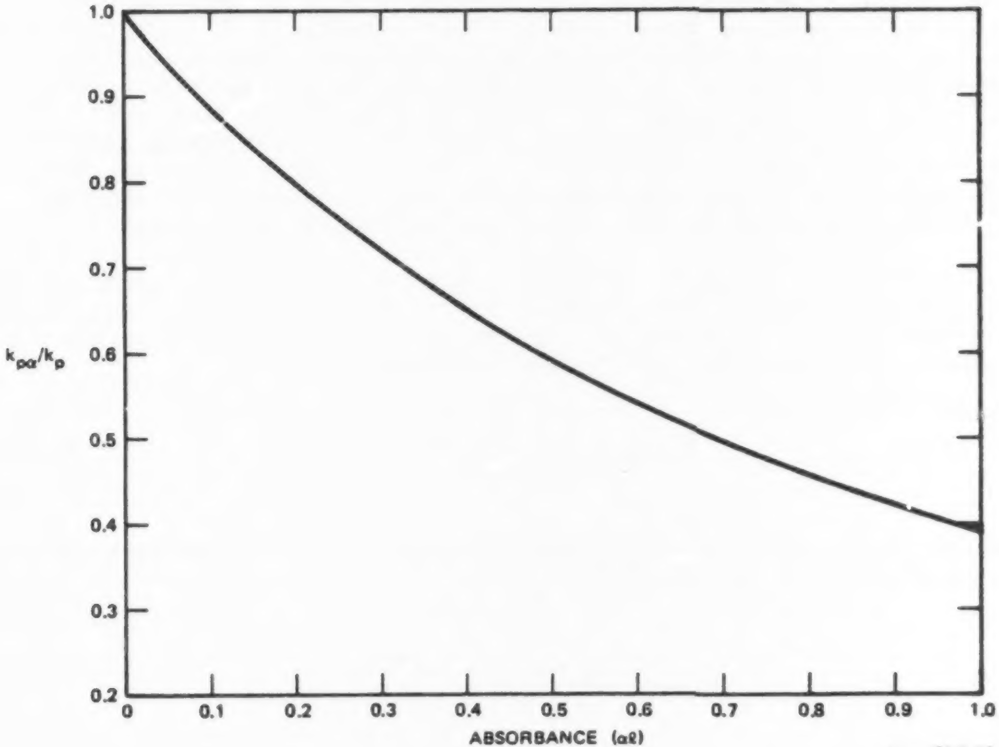

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FIGURE 3.2 PLOT OF LIGHT-SCREENING FACTOR, S, AGAINST ABSORBANCE FUNCTION (SEE SECTION 3.7.4)

Oxygen can also play a role in these reactions. A chemical that is unreactive on photolysis in pure water can be photolyzed in natural water; for example, aldrin to give dieldrin [Ross and Crosby (1975)], dimethylfuran to give diacetylethylene (Zepp et al., 1977) and cumene to give oxidation products (Mill et al., 1977).

Some discussion of the various indirect photolysis processes is useful to fully appreciate the role that photochemistry plays in the transformation of chemicals in the environment. One mechanism for indirect photolyses is a photosensitized reaction in which a sensitizer S (a compound or substance other than the chemical of interest) absorbs light, undergoes intersystem crossing from singlet to triplet excited state, and then transfers the excited state energy to the chemical, which undergoes reaction from the ${}^3C^*$ species:

$$S \longrightarrow {}^1S^*$$

$${}^1S^* \longrightarrow {}^3S^*$$

$${}^3S^* + C \longrightarrow S + {}^3C^*$$

$${}^3C^* \longrightarrow \text{Products}$$

The products of such sensitized reactions are often the same as if the chemical had absorbed the light itself in a direct photolysis process

$$C \xrightarrow{h\nu} {}^1C^*$$

$${}^1C^* \longrightarrow {}^3C^*$$

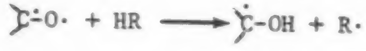
$${}^3C^* \longrightarrow \text{Products}$$

Thus, solvents (or cosolvents) that are sensitizers should be avoided in conducting photolyses to evaluate direct photolysis rate constants.

There is no unambiguous evidence that triplet-sensitized reactions of organics occur in natural waters. One reason for their possible unimportance is the rapid quenching of many triplets by oxygen with or without formation of singlet oxygen (${}^1O_2$).

$${}^3S^* + {}^3O_2 \longrightarrow {}^1S + {}^1O_2$$

Zepp et al. (1977) showed that 10^{-12} to 10^{-13} M $^1O_2$ was formed in a variety of natural waters with modest quantum yields ($\phi \sim 0.01$). Some triplets from carbonyls (n-π) are not as susceptible to quenching and may participate in free radical oxidations (Mill et al., 1977)



$$>\dot{C}-O\cdot + HR \longrightarrow >\dot{C}-OH + R\cdot$$

Subsequent reactions of $^1O_2$ and R· can form peroxides and other oxidation products. Thus, indirect reaction of triplets from natural organics seems clearly established.

The efficient quenching of some triplets by oxygen is also a possible source of retardation of some photolysis. For example, quinoline undergoes photolysis 2.3 times as fast in the absence of oxygen (Smith et al., 1978).

For the foregoing reasons, the photolysis protocols recommended in Sections 3.5 and 3.6 explicitly require use of air-saturated solutions of chemicals. Such conditions are relevant to shallow depths of pure water, and as long as the concentration of oxygen in the water (2.7×10^{-4} M) is constant, the effect of oxygen on the photolysis rate will be included in the reaction quantum yield and photolysis rates that are measured.

3.7.5 Photochemical Equipment

Sunlight Experiments

Numerous investigations of photolyses in sunlight have been described, but no uniform procedure is used. However, careful consideration of some variables that affect experimental results suggests some reasonable precautions for such experiments. Ideally, photolyzed solutions should be exposed in a sunlit location free from reflections from walls and windows and without morning or afternoon shadows. Solutions should be contained in a housing protected from weather; a greenhouse constructed of thin borosilicate glass, thermostated at about 25° ± 2°C, would be suitable for such sunlight experiments. In no case should solutions be exposed to freezing conditions.

Although large-diameter dishes with flat transparent tops (like petri dishes) most closely simulate the light conditions incident on a water body, such vessels are difficult to seal, and can lose both chemical or water through volatilization. Condensation of water or chemical on the lid may also serve to distort or absorb sunlight. These problems would be especially troublesome for experiments carried out for long reaction times, and would also make sampling difficult. Reasonable substitutes for reaction dishes are round borosilicate glass tubes, which can be prepared, sealed, and exposed to sunlight; one tube can be used for each time-datum point. The tubes should be placed in a rack at an angle of about 30° from vertical and positioned so that all tubes receive equal sunlight irradiation. If more accuracy is desired, the simultaneous photolysis of a solution of a nonvolatile, photoreactive chemical in a glass dish and glass tubes will provide reaction rates from which a tube correction constant can be calculated for use in studies on other chemicals. One study has found that photolyses in tubes are less than a factor of two faster than in dish containers (R. G. Zepp, private communication). Also, judging from the good agreement between photolysis rate constants measured in experiments using glass tubes and calculated from quantum yields and absorbance spectra (Smith et al., 1978), the glass tubes are quite satisfactory for environmental studies.

Laboratory Experiments

Design of Apparatus: The apparatus used to measure photochemical kinetics in the laboratory is usually of either the merry-go-round reactor or the optical bench design. Both designs provide for constant and even irradiation of a solution at a fixed distance from the light source and allow for interposition of a light-filter system between the light source and reaction solution. The general features of each design are described below, with the main components (light source, reaction cells, and light filters) described in separate sections. For both designs, the apparatus should be appropriately housed to shield laboratory personnel from exposure to uv light and to exclude extraneous light sources that could contribute to photoreaction of chemicals.

In the optical bench system, the light source is located at the end of the bench, usually with a housing around the light with an aperture to direct the light beam. The light then passes through glass filters or through a cell containing filter solutions that may transmit only one wavelength band. Filter solutions in the cell may be circulated through a cooling system, and the glass filters should be cooled with a stream of air to prevent heat buildup, which may crack the filters or cells. The reaction cell containing the solution of chemical is mounted coaxially with the lamp on the bench so that the filtered light enters the window of the cell. The reaction cell should be temperature-controlled to ± 2°C by circulating constant temperature water through side walls. A sufficient volume of reaction solution should be used to permit removal of samples for analysis without significantly altering the volume of the reaction solution in the cell. Details of construction of reaction cells may be found in Calvert and Pitts (1966) and deMayo and Shizuka (1976). Commercially available optical benches are preferred to ensure proper alignment of the components of the optical train, but simple "home-made" benches have been described (Andre et al., 1977).

The design of the merry-go-round reactor (MGRR) has been described in the literature (Moses et al., 1969; Murov, 1973; deMayo and Shizuka, 1977), and several designs are commercially available. The most common and practical design has the light source at the center of the MGRR in an immersion well with reaction solutions in tubes arranged in a ring around the light source. The ring rotates around the light source to give even irradiation of the reaction tubes. Glass filters may be inserted between the light source and the reaction tubes. Filter solutions may also be contained in the immersion well containing the light source or in a glass "donut" that surrounds the light source. To dissipate heat from the lamp, the MGRR may be immersed in a water bath or a stream of air may be passed through the space between light and filters; filter solutions can be circulated to an external cooling source. The design of the MGRR usually dictates that cells (cylindrical or square) of small volume can be used, with one cell used for each datum point measured.

The MGRR has the advantage over the optical bench that a number of samples can be irradiated at one time, and the apparatus takes up little laboratory space. The disadvanges of the MGRR are that it requires a larger initial investment to purchase or construct ($500 to $1,000) and the choice of lamps available for use in the MGRR is limited because of the fixed dimensions of the center well.

In summary, the MGRR and optical bench systems are both useful for measuring photochemical kinetics and quantum yields. Depending on the laboratory, the chemicals under investigation, and the number of measurements to be made, one system may be preferred over another.

Light Sources: A number of light sources with different intensities and wavelength distributions are available (Calvert and Pitts, 1966; deMayo and Shizuka, 1976; Murov, 1973). The use of an optical bench or MGRR will often narrow the choice of a lamp with regards to the use of a point source or a tube type lamp, since the former can be focused to give a collimated beam while the latter cannot. The main criterion for selecting a light source is that the lamp provides light at a constant and high intensity in a narrow wavelength region during the photolysis experiment. The output of the lamp should also be high enough to allow for attenuation of light by the isolation filter system and yet provide a high enough flux to perform the experiment within a reasonable time. DeMayo and Shizuka (1976) have suggested that, in general, for an experiment to be conducted in a reasonable time of 15 minutes to 10 hours, the intensity of the filtered light should be greater than 10^{14} photons cm^{-2} sec^{-1}. The lamp most commonly used in MGRRs is a 400-watt, medium-pressure Hg lamp. The characteristics and application of other lamps are presented in detail by Calvert and Pitts (1966), Murov (1973), and deMayo and Shizuka (1977). The last paper also discusses the use of lasers as light sources; if available, lasers are a convenient source of intense monochromatic light.

Light Filter Systems: Monochromatic or narrow wavelength light is essential for accurate measurements of photochemical quantum yields. Although a set of emission lines or a broad spectrum of light might be used to calculate a quantum yield, the absolute intensities at each wavelength would have to be known or calibrated continuously. The use of light in a narrow wavelength region is then more convenient, once the light source and filter system are set up in the MGRR or optical bench.

A narrow wavelength region is conveniently isolated with a combination of solution and glass filters; some of these combinations have been summarized by deMayo and Shizuka (1977), Murov (1973), and Calvert and Pitts (1966). As described earlier, these filter systems must be protected against excessive heat from the lamp. Although moderately expensive (> $50), glass interference filters very efficiently isolate narrow wavelengths of light. Glass filters that function by absorbing unwanted wavelengths of light are relatively cheap, quite stable and are recommended.

Filter solutions containing chemicals that absorb light in specific wavelength regions are also useful when glass filters are not available or are inapplicable to certain wavelength regions. However, since these solutions degrade on prolonged photolysis, they must be carefully monitored. Even when tap water is passed through the immersion well to cool the lamp, the buildup of solid material or algae in the well may reduce the light intensity. Repeated actinometry is the only method for detecting changes in output of the filtered light source.

Two filter systems commonly used for isolating the 313 nm and 366 nm bands from a 450-watt medium-pressure Hg lamp are described below:

- 313 nm filter system: Corning CS 7-54 glass filters with a 0.001 M potassium chromate solution in 3% aqueous sodium carbonate are circulated in an immersion well. This system transmits primarily the 313.2 and 312.6 nm Hg lines, which represent greater than 95% of the light incident on the reaction solutions (a small Hg line at 302.2 nm is also present).
- 366 nm filter system: Corning glass CS 0-52 and CS 7-60 glass filters are used. This pair of glass filters transmits only the 365.1, 365.6, 366.4 nm lines of the Hg lamp, with no other lines observed (less than 1% of light outside the 366 nm band).

When these filter systems were used in a MGRR with 10 cm between the light source and reaction solutions contained in 10 mm-O.D. borosilicate glass tubes, the light flux entering the solutions at 313 nm and 366 nm was about 5×10^{-6} einstein cm^{-2} sec^{-1} (Smith et al., 1977).

Reaction Cells and Solutions: Cells of large volume are appropriate for use with optical benches, and small cells are used with MGRRs. For quantum yield measurements relevant to environmental photochemistry, cells constructed of borosilicate glass are suitable because they transmit only light above 290 nm. To duplicate as closely as possible the optical chacteristics of the photochemical apparatus, actinometers and reaction mixtures should be photolyzed in identical reaction cells.

When actinometer solutions with optical densities greater than 2 are used, the cells should be examined after photolysis to determine whether solids have deposited on the walls of the cell as a result of a photoreaction at the cell-solution interface. Use of a more dilute solution of actinometer will remedy the problem. No problems of this kind have been encountered using ferrioxalate or nitrobenzaldehyde actinometers.

As mentioned earlier, the pathlength ℓ of a 1-cm-square cell is easily defined, but for a long path rectangular cell, and especially for a cylindrical cell where the light falls on rounded surfaces, the pathlength is less easily defined because of refraction and reflection in the cell. Zepp (1978) described an experimental method using an isolated wavelength band to determine the effective pathlength of any cell. Equation (3.59) is used in the pathlength calculation

$$-\frac{dC}{dt} = \text{Rate}_c = \phi I_{o\lambda} r(1 - 10^{-\varepsilon \ell c}) \qquad (3.59)$$

When $\varepsilon \ell C > 2$ (as in actinometry), equation (3.60) applies

$$\text{Rate}_{\text{max}} = \phi I_{o\lambda} r \tag{3.60}$$

where Rate_{max} is the maximum rate of disappearance for the chemical in the system (i.e., the light entering the cell is the rate-limiting factor). Division of equation (3.59) by equation (3.60) gives

$$\frac{\text{Rate}_C}{\text{Rate}_{\text{max}}} = 1 - 10^{-\varepsilon \ell C} = X \tag{3.61}$$

$$-\log(1 - X) = \varepsilon \ell C \tag{3.62}$$

Zepp (1978) measured the effective cell pathlength ℓ using the benzophenone-sensitized isomerization of cis-1,3-pentadiene. Described below are the steps followed in using equation (3.62) with the potassium ferrioxalate (FO) actinometer system at wavelength interval λ:

(1) Prepare FO solutions with OD > 2 with known concentration C_m.
(2) Prepare, by sequential dilutions of the solution above, FO solutions with optical densities 1 to 0.05 with known concentrations C_1, C_2, C_3, C_4, and C_5.
(3) Photolyze the six solutions for identical times in a MGRR and analyze for ferrous ion by standard procedures. Reaction times should be for less than 10% reaction of FO.
(4) Determine the ratios $\Delta C_1/\Delta C_m$, $\Delta C_2/\Delta C_m$, etc., where ΔC_1, ΔC_2, etc., are the amounts of ferrous ion formed in each respective photolysis. The ratios are designated X_1, X_2, etc.
(5) Plot the quantity $[-\log(1 - X_1)]$ versus $\varepsilon_\lambda C_1$, $[-\log(1 - X_2)]$ versus $\varepsilon_\lambda C_2$, etc., for each set of data points; ε_λ is the absorption coefficient for FO at λ.
(6) Calculate the slope of the plot, which is equal to the effective cell pathlength ℓ. A more accurate and precise value of ℓ may be obtained by a fit of the data by linear regression analysis.

We have found that a cylindrical borosilicate reaction tube* with an I.D. of 11.0 mm and an O.D. of 13.0 mm has an effective pathlength of 11.2 mm. A reaction tube made from borosilicate glass stock of I.D. 9.7 mm and O.D. 12 mm had an effective pathlength of 10.0 mm.

---

*The tubes are Corning Glass disposable culture tubes, 13 x 100 mm and are especially convenient because they have screw caps for easy sealing.

Other workers have pointed out that when actinometry is carried out in cylindrical cells the light flux measured (and therefore any quantum yields) will be solvent dependent because of the refractive indices of the solvent. Thus the quantum yields for photoisomerization of 1,3-pentadiene in benzene were 0.64 and 0.55 when ferrioxalate (in water) and benzophenone-benzhydrol (in benzene), respectively, were the actinometers used (Vesley, 1971). The reason for the difference was attributed to the difference in refractive indices of water and benzene. Benzene has a refractive index ($n^{20^\circ} = 1.501$) similar to glass and allows all incident light to pass into solution, whereas water ($n^{20^\circ} = 1.332$) refracts and reflects some of the light at the inner cell walls. The aqueous ferrioxalate actinometer therefore underestimated the light that actually entered the solution in the cell when benzene was the solvent and thus overestimated the true quantum yield for pentadiene isomerization by 15%.

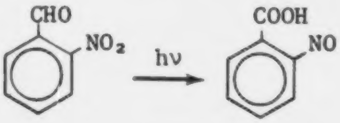
Since the quantum yields of interest in these protocols are for aqueous solutions, actinometry should be performed in aqueous solutions whenever possible. In cases where aqueous actinometers are not practical, an actinometer solvent such as acetonitrile ($n^{20^\circ} = 1.344$) may be suitable.

3.7.6 Actinometers and Actinometry

Actinometers are chemicals that photolyze in solution over a wide spectral range with well-known quantum yields that change little with wavelength and produce products that are easily measured. Two examples are potassium ferrioxalate in water

$$2Fe^{+++} + C_2O_4^{=} \xrightarrow{h\nu} 2Fe^{++} + 2CO_2$$

and o-nitrobenzaldehyde in acetonitrile



Neither reaction is affected by oxygen and only slightly by temperature; therefore, these reactions can be used to measure reliably the light flux entering a reaction cell.

Typically, a solution of actinometers of known optical density and path length is exposed to the light source for a known period of time and then analyzed for product. Since most actinometers have high quantum yields, even low photon fluxes will make 1% to 2% changes in short times and require exclusion of stray light during preparation and analysis. The incident photon flux is calculated using equations (3.43), (3.45), or (3.47) and solving for $I_{o\lambda}r$, using the known value of ϕ. Precisions of ± 10% are usual in this determination. Although the common practice has been to use highly absorbing solutions of actinometers to ensure that all light is absorbed and zero-order kinetics is obeyed (equation 3.4 7), there is no reason that more dilute solutions cannot be used, provided the correct kinetic equation is used to determine $I_{o\lambda}r$.

Because of the low quantum yields in environmental photochemistry, it is frequently necessary to use protracted exposure times of chemicals to achieve significant reaction. Actinometry must then be carried out at frequent intervals to ensure that the light flux has not changed. In practice, this usually means that actinometry is performed once at the beginning of the experiment and once at or near the end.

Excellent descriptions and instructions on the use of some known high-optical-density actinometers are available (Demas, 1976; deMayo and Shizuka, 1976; Calvert and Pitts, 1965; Murov, 1973). Of the actinometers cited by these authors, the actinometers in aqueous solution are the most useful for environmental studies because of the solvent-refractive index problem discussed above (Section 3.7.5). All the aqueous actinometers are metallo-organic redox reactions. Only o-nitrobenzaldehyde in acetonitrile solvent also appears to be useful for environmental photochemical studies.

As pointed out by Zepp (1978) and Demas (1977), dilute solution actinometers have several practical advantages over high-optical-density actinometers but none of the dilute solution methods can be considered well enough established for routine use at this time.

Few chemicals are available for use as reference standard chemicals for sunlight photolyses. Most common laboratory actinometers react far too rapidly in sunlight to be of practical use as sunlight actinometers. While it is provisionally acceptable to use chemicals that have been shown to give good correlation between measured and calculated sunlight photolysis rates (Zepp and Cline, 1977; Zepp, 1978; Smith et al., 1977), more data on the chemistry occurring in such systems would provide more reliability for general use. Certainly more sunlight experiments are necessary to verify half-lives calculated as a function of the time of year and latitude.

3.7.7 Light Sources to Simulate Sunlight

Several systems described in the literature (Koller, 1965) simulate sunlight in a qualitative manner. These light sources are either lamps with no output below 300 nm or coupled with filters (most commonly borosilicate glass) to block light below 300 nm. Except for the xenon lamp, none of the laboratory sources closely approximates the intensity and distribution of sunlight over the entire solar spectrum in a manner suitable for general application to estimating environmental photolysis rates. Xenon lamps require expensive auxiliary equipment; moreover, while all lamps show some decay in light output with time, xenon lamps are particularly prone to decay. Lamps with a broad spectrum output above 300 nm have an additional drawback in quantitative applications in that they must be continuously calibrated for comparison with sunlight, and no inexpensive and simple procedure is available at this time. Since the photon flux is the important property of light related to reaction rate, a simple measurement of the energy output of a lamp over a broad region is not an acceptable way of relating the output of a laboratory lamp to sunlight (see Section 3.7.5).

3.7.8 Sunlight Intensity Variations

A major variable in the sunlight photolysis rates of chemicals in the aquatic environment is the intensity and wavelength distribution of sunlight itself, which varies with the time of day, season, and latitude. The intensity and distribution of light energy in the atmosphere has been discussed by Leighton (1961), Koller (1965), Bener (1972), and Peterson (1976). These authors treat sunlight observed at the earth's surface and in the troposphere as composed of two components. One component is the direct light from the sun, which has an intensity that is dependent on the angle of the sun in the sky. The other component is sky light, of uniform intensity, which results from light scattering in the sky. Zepp and Cline (1977) have used the data of Bener (1972) and Leighton (1961) in their computer program to calculate photolysis rate constants in aquatic systems.

Although cloud cover, air pollution, ambient particulate, and other transient conditions reduce the incident sunlight intensity and can cause significant fluctuations in solar flux, the effect of such transient or localized conditions cannot be reliably included in estimations of sunlight intensity. The need for a general and uniform set of data for sunlight photolysis rate constants requires that clear-sky light intensity data be used; however, the user of such data should be aware of error limits of the rate constants obtained with the data (see Error Analysis, Section 3.6.8).

Strong support for using the clear-sky intensity data has been provided by the good agreement obtained between photolysis rate constants measured in sunlight experiments and those calculated using quantum yields and absorbance spectra for several pesticides (Zepp, 1978) and for polynuclear aromatic hydrocarbons and heterocycles (Smith et al., 1978). The agreement found for rates of photolysis of several of these chemicals (Smith et al.) is shown graphically in Figure 3.3. Zepp and Cline's program calculates rate constants as a function of the time of day or averaged over a full day, with good agreement found again as shown in Figure 3.3 for midday or day-averaged photolysis half-lives.

The program of Zepp and Cline can also calculate photolysis rate constants and half-lives as a function of dates and latitude. Calculated half-lives for two compounds are shown in Tables 3.7 and 3.8 and show the effect of changes in latitude and season on the rates at which chemicals photolyze in sunlight.

Benzo[a]pyrene shows a 2.2-fold change in rate at 40° latitude between winter and summer, whereas methyl parathion shows a 3.8-fold change in rate for the same latitude and seasons. Methyl parathion is more dependent on the low wavelengths of sunlight for photolysis than benzo[a]pyrene and therefore shows a greater difference between winter and summer than benzopyrene because of the greater variation in shorter wavelength light flux between the two seasons.

A problem that occasionally arises in some photolysis experiments is how a chemical that has "no extinction coefficient" (or at least none detectable) in the solar spectral region may be found to photolyze when exposed to sunlight (Rosen, 1972). Some reasons suggested for this behavior have been: a small amount of sunlight below 290 nm that penetrates the earth's atmosphere (Barker,

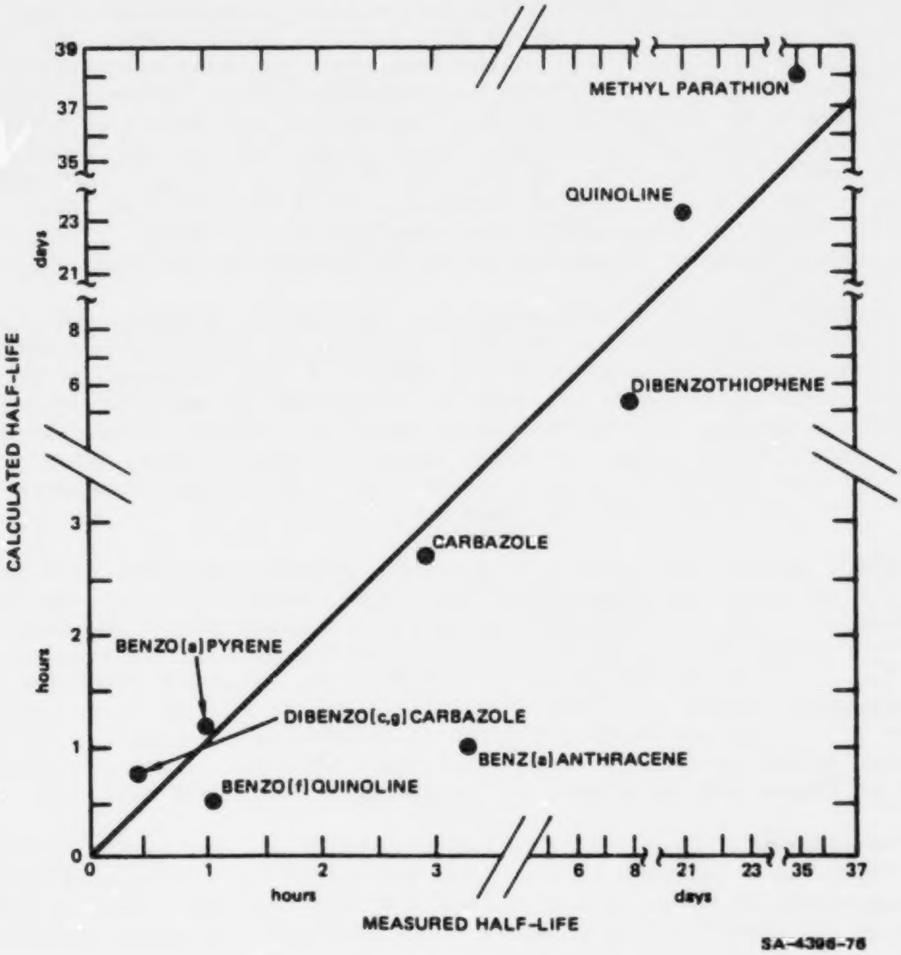


FIGURE 3.3 COMPARISON OF MEASURED AND CALCULATED HALF-LIVES FOR DIRECT PHOTOLYSIS

TABLE 3.7. BENZO [a] PYRENE PHOTOLYSIS HALF-LIVES (hours)
(Calculated for Midday)

	Season Date			
Latitude	Spring	Summer	Fall	Winter
0	0.52	0.53	0.51	0.53
10	0.47	0.52	0.53	0.58
20	0.52	0.50	0.58	0.68
30	0.54	0.52	0.68	0.85
40	0.58	0.54	0.85	1.2
50	0.68	0.59	1.21	2.1
60	0.85	0.68	2.09	4.8
70	1.22	0.85	4.72	---

TABLE 3.8. METHYL PARATHION PHOTOLYSIS HALF-LIVES (days)
(Calculated for 24-Hour Calendar Day)

	Season Date			
Latitude	Spring	Summer	Fall	Winter
0	9.2	9.60	9.00	9.5
10	5.6	8.84	9.73	11.0
20	9.1	8.48	11.1	13.8
30	9.6	8.45	13.6	19.1
40	10.7	8.68	18.1	30.7
50	12.7	9.24	27.7	61.6
60	16.0	10.2	51.4	190
70	21.8	11.4	144.	--

1968), changes in the absorption spectrum of the chemical as a result of surface interactions, or adventitious reactions with oxidants or photosensitizers. While such processes are possible, direct photolysis of a chemical also may occur if the reaction quantum yield (ϕ_c) is high enough to compensate for low absorption coefficients (equation 3.55). For example, assuming that a chemical has constant absorption coefficients ε_λ equal to 0.1 M^{-1} cm^{-1} in the wavelength region 296 to 320 nm and $\phi = 1$, the calculated half-life is 120 days in summer at 40° latitude. If the wavelength region extends to 360 nm with ε_λ constant at 0.1, the calculated half-life is 12.0 days in summer. Thus, the ability to predict, or even to rationalize environmental photolysis rates for some chemicals may depend on the state of instrumentation for measuring absorption coefficients accurately below 0.1 M^{-1} cm^{-1}.

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Appendix 3.A

CALCULATION OF L_λ VALUES

In a water body exposed to the sun, the intensity of light passing into the water body is ($I_{o\lambda}$) is composed of light directly from the sun ($I_{d\lambda}$) and the light from the sky ($I_{s\lambda}$). Leighton (1961) discussed the calculation and contribution of $I_{d\lambda}$ and $I_{s\lambda}$ to the total light intensity at a point on the earth's surface as a function of the zenith angle z (Figure 3.A.1). Zepp and Cline (1977) extended the discussion to the $I_{d\lambda}$ and $I_{s\lambda}$ components that enter the water body, and the reader is referred to this paper for a more complete discussion of the subject.

Zepp and Cline showed that the pathlength, ℓ_d, of direct radiation in a water body is

$$\ell_d = D \sec \Theta \qquad (3.A.1)$$

where D is the depth, Θ is the angle of light refraction from vertical in the water body (Figure 3.A.1), defined by $\sin z - n \sin \theta$ where n is the index of refraction of water and z is the angle of the sun from vertical. Assuming that the sky is uniformly bright and neglecting reflection from water, the pathlength ℓ_s of sky radiation in water is

$$\ell_s = 1.20\ D \qquad (3.A.2)$$

if the index of refraction of water is taken as 1.34. Allowing for the individual intensity and pathlength terms for the direct and sky radiation, the term for $I_{o\lambda}\ell$ in a water body becomes

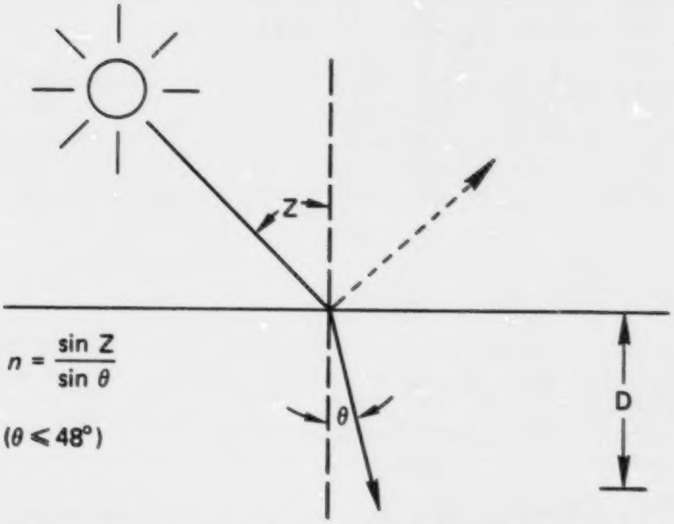
$$I_{o\lambda}\ell = I_{s\lambda}1.20D + I_{d\lambda}D \sec \Theta \qquad (3.A.3)$$

The general equation for photolysis in water (see page 30)

$$-\frac{dC}{dt} = \frac{\phi I_{o\lambda}}{D}\,[1 - 10^{(\alpha_\lambda + \varepsilon_\lambda C)\ell}]\left[\frac{\varepsilon_\lambda C}{\varepsilon_\lambda C + \alpha_\lambda}\right] \qquad (3.A.4)$$

may be considerably simplified by two assumptions. First, when the chemical absorbs only a small fraction of the light compared with the water body, $\varepsilon_\lambda C\ell << \alpha_\lambda \ell$, then

$$\begin{aligned} -\frac{dC}{dt} &= \frac{\phi I_{o\lambda}}{D}\,\frac{\varepsilon_\lambda}{}\left[1 - 10^{-\alpha_\lambda \ell}\right]\frac{[C]}{\alpha_\lambda} \qquad (3.A.5) \\ &= \phi\frac{\varepsilon_\lambda}{D\alpha_\lambda}[I_{o\lambda}(1 - 10^{-\alpha_\lambda \ell})]C \end{aligned}$$



$$n = \frac{\sin Z}{\sin \theta}$$

$(\theta < 48°)$

Z = Angle of incidence (solar zenith angle in case of direct sunlight)
θ = Angle of refraction
n = Refractive index of water

SA-4396-77

FIGURE 3.A.1 REFLECTION AND REFRACTION OF A LIGHT BEAM PASSING FROM ATMOSPHERE INTO A WATER BODY
(From Zepp and Cline, 1977)

Second, when $\alpha_\lambda \ell < 0.02$, as is the case near the surface of water,

$$k_p = 2.3\, \varepsilon_\lambda \phi I_{o\lambda} \ell / D \qquad (3.A.6)$$

Substitution in (3.A.6) for $I_{o\lambda}\ell$ from equation (3.A.3) gives

$$k_p = 2.3\, \varepsilon_\lambda \phi [1.2\, I_{\lambda s} + I_{d\lambda} \sec \Theta] \qquad (3.A.7)$$

Thus k_p becomes independent of depth near the surface.

Since the protocol is to be applied to environmental photolysis rates where the primary concern is for chemicals with half-lives of days or months rather than hours, the total light intensity (in brackets in equation 3.A.7) should be an averaged light intensity for an entire day. This light intensity term is called L_λ and was obtained as described below.

Zepp and Cline (1977) have written a computer program that calculates the first-order sunlight photolysis rate constants k_p for 39 specific wavelength intervals from 296.3 to 825 nm and then sums these rate constants to obtain the environmental rate constant k_{pE}. The computation is based on equation (3.A.5) in which $I_{o\lambda}$ is substituted by equation (3.A.3)

$$k_p = \frac{\phi \varepsilon_\lambda}{\alpha_\lambda D} [I_{s\lambda}(1 - 10^{-\alpha_\lambda \ell_s}) + I_{d\lambda}(1 - 10^{-\alpha_\lambda \ell_d})] \qquad (3.A.8)$$

and requires input data of ϕ and ε_λ. Data for α_λ, depth and other parameters can also be included for calculating photolysis rate constants and half-lives under a number of environmental conditions. The $I_{s\lambda}$ and $I_{d\lambda}$ values themselves are based on the data of Bener (1972) and Leighton (1961) and are calculated as a function of season, time of day, and latitude.

The output of the program provides the instantaneous rate constants at specific times of the day for a given latitude and season date. The term midseason date as used by Zepp and Cline does not refer to a day midway in the season, but rather a day during the season when the angle of declination of the sun is at the specific values used in the computer program; in the text, we have referred to these days as "season dates" to avoid misinterpretation of the word "midseason." See Section 3.6.4 for further information on the season dates for the four seasons. The program further calculates a photolysis rate constant k_{pE}, which is averaged over a 24-hour calendar day (with k_{pE} in units of day^{-1}).

To obtain L_λ date data for use in equation (3.A.8), we calculated the day averaged, season photolysis $k_{p\lambda}$ values, using the computer program with ε_λ equal to unity and the absorption coefficients α_λ for pure water. The $k_{p\lambda}$ values with ϕ and $\varepsilon_\lambda = 1$ are designated L_λ. The units for L_λ are einsteins 10^{-3} cm^{-2} day^{-1}. Multiplication of L_λ by an actual ε_λ (in M^{-1} cm^{-1}) then gives the first-order rate constant $k_{a\lambda}$, (in day^{-1}) since einsteins liter^{-1} is equivalent to M.

Since the L_λ values were calculated using the program of Zepp and Cline the difference between the Z_λ values in their paper and the L_λ values presented here should be clearly defined. Most importantly Z_λ values pertain to midseason, midday light intensity and are used to calculate midday, midseason photolysis rate constants. L_λ data are used to calculate day-averaged, 24-hour (calendar) day photolysis rate constants. Also, units of L_λ and Z_λ are different.

It is instructive to compare the assumptions underlying the L_λ and Z_λ values. To obtain Z_λ values, Zepp and Cline used equation (3.A.7) as the starting point and defined

$$Z_\lambda = (1.2\ I_{s\lambda} + I_{d\lambda}\ \sec\theta) \qquad (3.A.9)$$

in units of photons cm^{-2} sec^{-1}. They define the instantaneous photolysis constant in sunlight at midday, midseason in terms of Z_λ as

$$k'_{pE} = \frac{2.3}{J}\,\phi \sum . z_\lambda \varepsilon_\lambda \qquad (3.A.10)$$

which differs from equation (3.A.8) by the conversion factor J (photons/einsteins) and by the units of cm^{-2} sec^{-1} instead of $liter^{-1}$ day^{-1}.

Appendix 3.B

INTEGRATION OF EQUATION (3.40)

Equation (3.40)

$$-\frac{dC}{dt} = \phi I_{o\lambda} r[1 - 10^{-\varepsilon_\lambda C\ell}]$$

is readily integrated. For convenience in integration, substitution is first made of terms $a = \phi I_{o\lambda} r$ and $b = 2.3\ell\varepsilon_\lambda$ to give

$$-\frac{dC}{dt} = a(1 - e^{-bC}) \tag{3.B.1}$$

Integration of equation (3.B.1) then gives

$$a\int_{t_o}^{t} dt = \int_{C_o}^{C_t} \frac{dC}{e^{-bC} - 1} = \int_{C_o}^{C_t} \frac{e^{bC}\,dC}{1 - e^{bC}} \tag{3.B.2}$$

$$at\Big]_{t_o}^{t} = -\frac{1}{b} \ln (1 - e^{bC})\Big]_{C_o}^{C_t} \tag{3.B.3}$$

where C_o and C_t are chemical concentrations at times t_o and t, respectively.

Then

$$a(t - t_o) = -\frac{1}{b} \ln \frac{(1 - e^{bC_t})}{(1 - e^{bC_o})} \text{ or } = -\frac{1}{b} \ln\left(\frac{e^{bC_t} - 1}{e^{bC_o} - 1}\right)$$

When $t_o = 0$, equation (3.B) then gives

$$-bat = \ln(e^{bC_t} - 1) - \ln(e^{bC_o} - 1) \tag{3.B.5}$$

CHAPTER 4. OXIDATION IN WATER

by

T. Mill

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4. OXIDATION IN WATER

4.1 INTRODUCTION

Chemical oxidation is often observed in aquatic environments as a consequence of photochemical processes which generated free radicals by bond homolysis of electronically excited species or singlet oxygen by energy transfer from an electronic triplet state to triplet oxygen. Two general types of oxidation reactions can be distinguished for evaluating chemical oxidation processes in an aquatic environment:

(1) Reaction of an excited state of a molecule with oxygen, in which the excited state is produced by direct photolysis or by interaction with a photosensitizer; this process is termed photooxidation
(2) Reaction of the ground state of the chemical with oxidants in solution, in which the oxidants are formed by reactions of dissolved or suspended natural materials in solution; these reactions are termed thermal oxidation, autoxidation or simply oxidation. The ultimate driving force for oxidant formation may, however, often be photochemical reactions of the natural materials.

This distinction between photooxidation and thermal oxidation is important if laboratory test procedures are to be developed that will accurately predict the rates of these processes in a variety of aquatic environments. In most cases the properties of a chemical and of an aquatic environment that must be characterized are quite different for these two kinds of processes. Scheme 1 illustrates the two processes and the rate laws that govern them. In photooxidation the relevant molecular and environmental properties are the absorption coefficient in the solar region, quantum yield, and solar irradiance. In thermal oxidation the relevant properties are rate constants for oxidant-molecule reactions, oxidant concentrations, and temperature.

This report is concerned only with thermal oxidation (hereafter termed simply oxidation). Test methods are proposed for evaluating the rate constants for oxidation based on theoretical and experimental methods used in oxidation chemistry. Literature and current research on oxidation processes have been reviewed, and the most reliable methods for predicting rates of oxidation in aquatic systems are discussed.

4.2 OBJECTIVE

The objectives of this research are to develop simple reliable test procedures for measuring rate constants for oxidation of most types of chemicals dissolved in water at 25°C and for using these data to predict the rates of oxidation in aquatic systems.

Scheme 1

PHOTOOXIDATION AND THERMAL OXIDATION

Photooxidation

$$AY + h\nu \longrightarrow AY^*$$

$$AY^* \longrightarrow A\bullet + Y\bullet$$

$$AY^* + O_2 \longrightarrow \text{Products} \quad \text{(several steps)}$$

or

$$Y\bullet \text{ or } A\bullet + O_2 \longrightarrow \text{Products} \quad \text{(several steps)}$$

$$R_{OX} = \phi I_\lambda \varepsilon_\lambda [AY]$$

Thermal Oxidation

$$AY + OX \longrightarrow \text{Products} \quad \text{(several steps)}$$

$$R_{OX} = k_{OX}[AY][OX]$$

(OX is any oxidant)

4.3 SUMMARY

This report recommends that two screening tests be used to evaluate the rate constants for oxidation of selected chemicals by alkylperoxy radicals ($RO_2\bullet$) and by singlet molecular oxygen ($^1O_2$), both of which are found in natural water exposed to sunlight. Two screening tests were developed to provide approximate values of these rate constants. No detailed tests are recommended at this time owing to a lack of information on kinetic processes and on standard chemicals needed for relative rate measurements.

Background information on kinetics rate laws for oxidation processes has been developed in order to use rate constants for oxidation, estimated from screening tests, for calculating the persistence of chemicals in natural aquatic systems. The concentrations and reactivities of oxy free radicals and singlet oxygen are such that only $RO_2\bullet$ and $^1O_2$ are likely to be important oxidants in natural waters and only selected classes of chemicals are going to be reactive enough toward these oxidants to justify use of screening tests for oxidation.

These reactive chemicals include: phenols, aromatic amines, thiols, hydroxylamines, and hydrazines, all of which are reactive toward $RO_2\bullet$; eneamines, vinyl ethers, internal olefins, furans, dienes, polycyclic aromatics, and sulfides, all of which are reactive toward $^1O_2$.

The chemistry and kinetics of $RO_2\bullet$ reactions have been well worked out in non-aqueous solvents. Peroxy radicals mostly transfer H-atoms or add to double bonds. The rates of H-atom transfer are usually slow from CH bonds, $k_{RO_2} < 100\ M^{-1}\ s^{-1}$, and usually rapid from ArOH, ArNH and RSH bonds, $k > 10^4\ M^{-1}\ s^{-1}$. Singlet oxygen undergoes five distinctive types of reactions: 1,2- and 1,4-cycloaddition, ene reaction, sulfide oxidation and electron transfer; these reactions vary in rate over five orders of magnitude.

Solvent and temperature effects for both oxidants are expected to be small enough to minimize the need for close temperature control and allow use of mixed water-organic solvents at least for $^1O_2$ reactions.

4.4 CONCLUSIONS AND RECOMMENDATIONS

Selected classes of organic chemicals exhibit sufficiently high reactivity toward $RO_2\bullet$ or $^1O_2$ to warrant belief that these oxidants could play important roles in aquatic loss processes for some chemicals. Therefore screening tests for preselected chemicals are needed and test methods are proposed. Preselection of molecular structures reactive enough to justify oxidation screening tests is based on the assumption that any chemical that exhibits a half-life for oxidation in an aquatic environment in excess of 80 days need not be tested further. Very unreactive chemicals may exhibit longer half-lives toward all transformation processes, in which case this 80-day limitation will not hold. The test method proposed for oxidation of ArOH or ArNH bonds by $RO_2\bullet$ gives only a lower limit to the rate constant.

Additional experimental and theoretical work will be necessary on the kinetic processes involving $RO_2\bullet$ oxidations of -NH, -OH or -SH before satisfactory tests for these reactions can be developed. No satisfactory standard chemicals for relative reactivity measurements are now available for either $RO_2\bullet$ or $^1O_2$ oxidations.

We recommend that some additional work be done to improve the screening level tests and provide the basis for detailed tests if they are needed.

Specifically, we recommend that the following studies be carried out:

- Survey computer lists of currently manufactured chemicals to determine the fraction of chemicals that have reactive phenolic or amine functions to better evaluate the relative importance of oxidation among transformation processes.
- Conduct both experimental and modeling studies to evaluate kinetic parameters for oxidation of ArNH or ArOH bonds in water to better design test methods.

4.5 SCREENING TEST

The purpose of screening tests is to provide approximate values of rate constants and or half-lives for reaction of a chemical with peroxy radical and singlet oxygen. Half-lives may then be used in comparing the importance of oxidation with other loss processes.

Since only a relatively small proportion of all chemicals will have reactive functionalities it is important that the investigator evaluate carefully the probable reactivity before deciding to screen or not screen. The range of reactivity for which screening is needed, as shown in Schemes 2A and 2B, is based on a half-life of 80 days in the environment; chemicals with rate constants that will lead to half-lives greater than 80 days in aquatic systems should not ordinarily be screened. Exceptions to this rule will arise only if all other aquatic processes are found to have half-lives greater than 80 days, in which case the investigator must reconsider the question of screening for oxidation.

4.5.1 Screening Test for Peroxy Radical Oxidation of CH Bonds

Materials needed for this procedure are:

(1) Solution A: a solution of the chemical in pure water at a known concentration below one-half of its solubility limit and at or below 1 x 10^{-4} M.
(2) Solution B: a solution of 2 M t-butyl hydroperoxide (t-BuO_2H) in pure water.
(3) Solution C: a solution of MAB[†] in water at (3.00 ± 0.5) x 10^{-4} M.
(4) A constant temperature bath large enough to hold three 50-ml tubes and regulated to 50 ± 1°C.

The test is carried out as follows: equal volumes of the solutions A-C are mixed in several 10 to 50-ml volumetric flasks or tubes at room temperature, avoiding direct sunlight. Another of volume solution A is mixed with equal volumes of solution B and pure water as control 1. All reaction tubes are sealed without grease.[‡] One or two reaction mixtures are covered with metal foil to exclude light entirely and are set aside in a cool place as control 2. The other reaction tubes and control 1 are immersed in the bath at 50°C and the time is noted. After 10 hours (time noted exactly), the tubes are removed, immediately cooled, and stored in the refrigerator with control 2 until they are analyzed. Controls 1 and 2 are analyzed in duplicate first to obtain the

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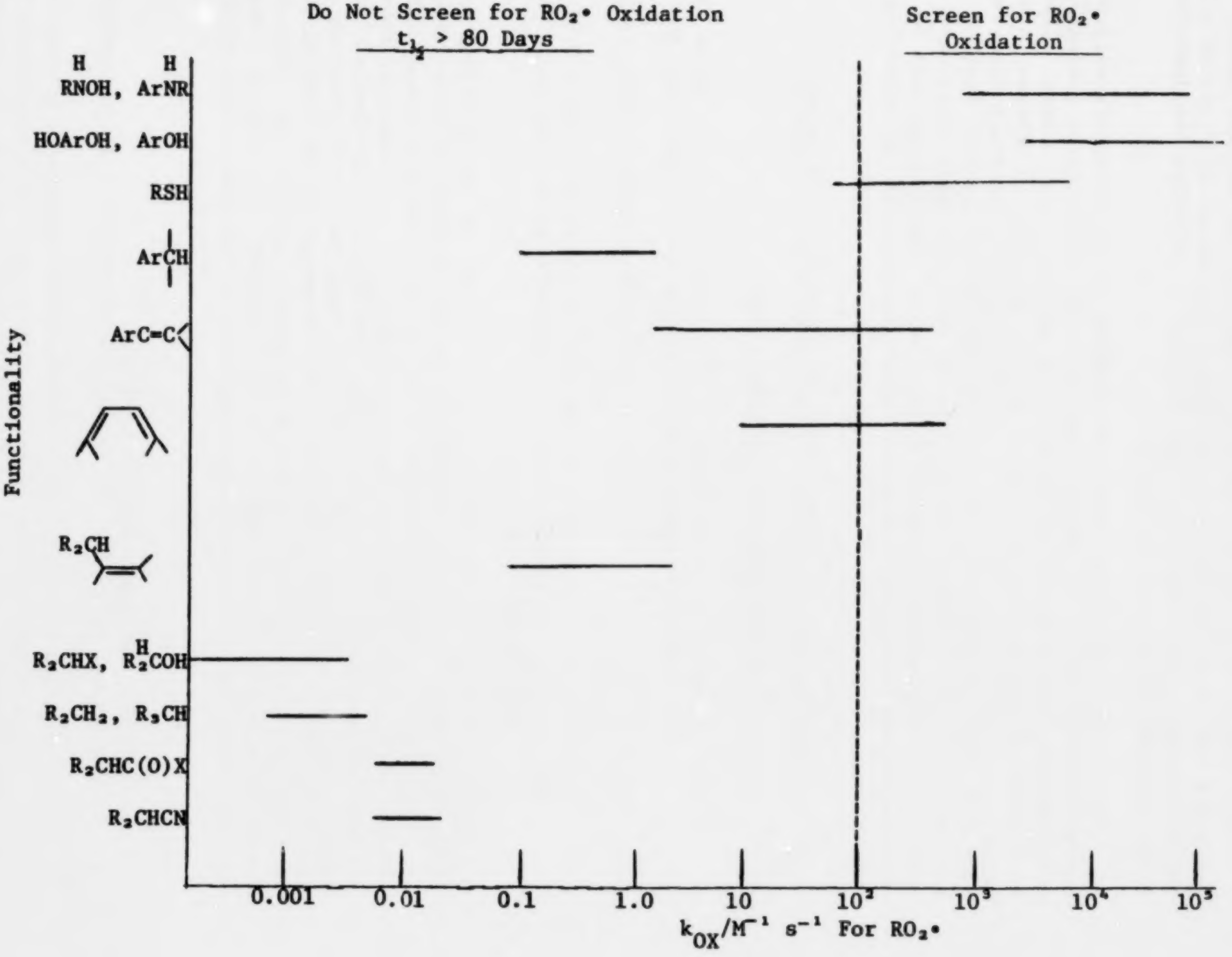
[*] To be used only for very reactive CH bonds.

[†] MAB is our abbreviation for the azo initiator azobis(2,2'-carboxymethyl propane).

[‡] A screw cap flask having an inert plastic valve (Minnert®, Pierce Chemical) fitted into the cap is a useful means of sealing flasks containing volatile chemicals dissolved in water. The valve can be opened as the temperature is raised to allow for expansion of liquid, closed at the elevated constant temperature, and then reopened later for sampling.

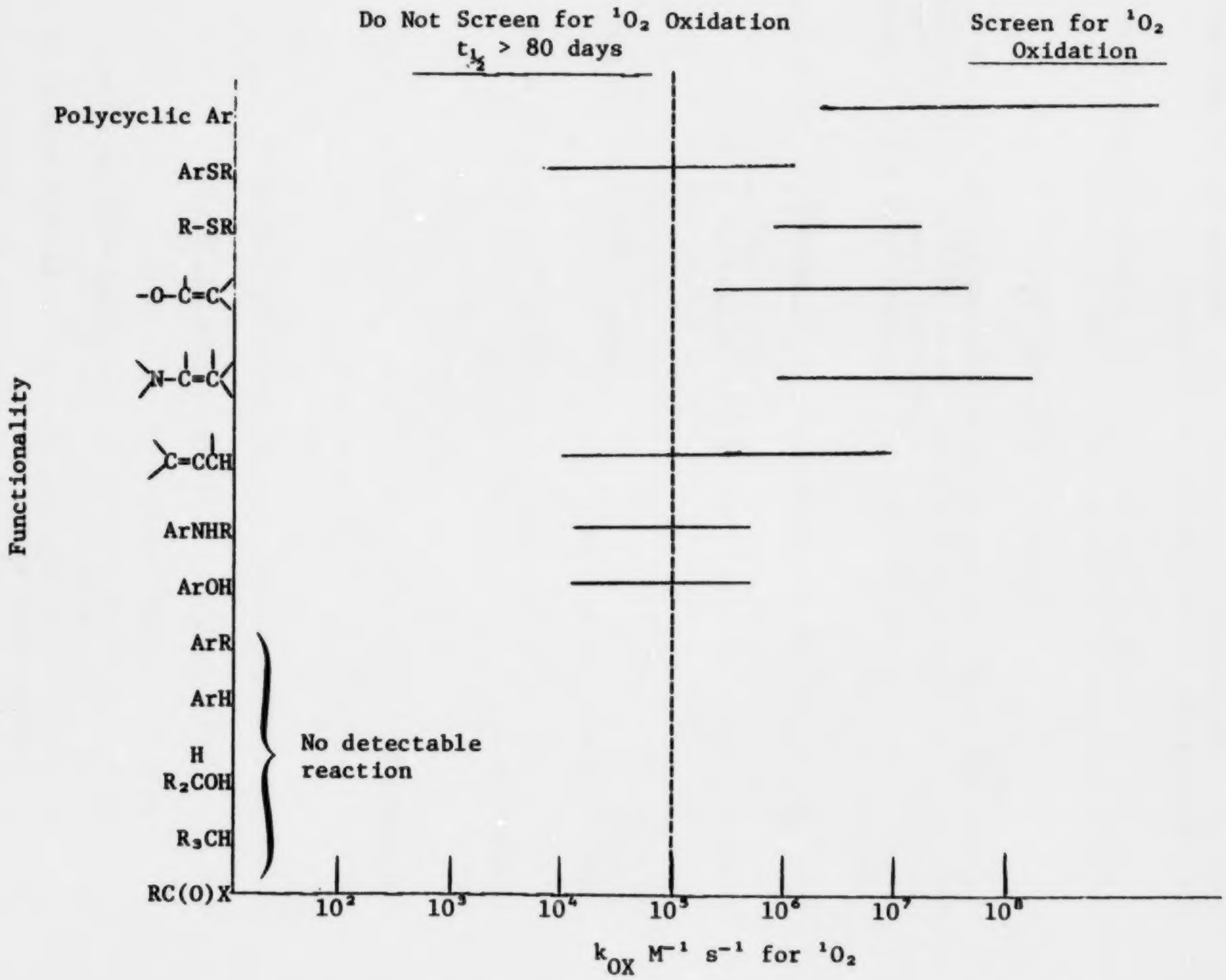
Scheme 2A

Classification for Screening Toward $RO_2\cdot$



Scheme 2B

Classification for Screening Toward $^1O_2$



concentration of chemical at zero time. These control concentration values should be nearly the same; if not, additional experiments may be necessary to find the source of the discrepancy, especially if control 1 has a smaller concentration than 2 (in this case $t\text{-}BuO_2H$ has probably reacted directly with the chemical). The heated solutions are then analyzed in the same way to measure the concentration of the chemical at 10 hours.

The half-life of the chemical in an aquatic environment at 25°C is calculated using the following formula (Section 4.7.3)*

$$t_{\frac{1}{2}}(\text{days}) = 4500/\ln(C_o/C_t) \qquad (4.1)$$

where C_o and C_t are concentrations of chemical at time zero and t (days). If equation (4.1) gives a half-life for the chemical of more than 80 days, oxidation by $RO_2\bullet$ is not likely to be an important process for its loss in aquatic systems, and no additional tests are necessary until other screening tests are complete.

4.5.2 Screening Test for Oxidation of ArOH, ArN(H)R or RSH by $RO_2\bullet$

The materials needed for this procedure are solutions A and C and a constant temperature bath. The test is carried out as follows: equal volumes of solutions A and C are mixed as described above for the oxidation of CH bonds. Control solutions are prepared from solution A and an equal volume of pure water or water and acetonitrile. Several controls and several reaction mixtures are heated at 50 ± 1°C for 20 hours. Solutions are analyzed for ArOH (ArN(R)H or RSH) as described above.

The half-life in the environment at 25°C is calculated using the following formula: if $C_t/C_o \lesssim 0.75$, then $k_{OX} \geq 10^4\ M^{-1}\ s^{-1}$ and in the environment

$$t_{\frac{1}{2}} \leq 19 \text{ hr}$$

Conversely if $C_t/C_o \geq 0.75$, then $k_{OX} \leq 10^4\ M^{-1}\ s^{-1}$ and in the environment

$$t_{\frac{1}{2}} \geq 19 \text{ hr}$$

No detailed test procedure is recommended at this time.

4.5.3 Screening Test for Oxidation by Singlet Oxygen

Materials needed for this procedure are:

- Solution A of chemical in pure water or in 90:10 water: acetonitrile at a concentration of 1×10^{-4} M.
- Solution B of standard chemical in the same solvent as for the test chemical also at 1×10^{-4} M.
- Solution C of rose bengal sensitizer at 2×10^{-4} M in the same solvent as solutions A and B.
- A merry-go-round photolysis unit or visible light source and mounting for reactions cells.

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*This equation is based on equation 4.34; The derivation is available on request.

The test procedure is carried out as follows: equal 25 ml volumes of solutions A and B are mixed and one ml of solution C is added and mixed. A control solution is prepared by mixing equal volumes of solutions A and B only. One sample of the control solution is set aside in the dark. Enough of the reaction mixture and the control solution are placed in the photolysis reactor to allow four samples of each to be withdrawn for analyses over a period of 100 hr while being photolyzed. The first withdrawal should occur at 1 hr and if more than 15% of the chemical and reactant have disappeared from the reaction mixture and none from the control, the photolysis should be terminated. If more than 15% of only one component has reacted in 1 hour, then photolysis should continue until the more than 15% of the other component (reference or chemical) has reacted. Time should be noted exactly at each sample withdrawal. Conversions of more than 50% of either component should be avoided.

Treatment of the data obtained is straightforward: the half-life for oxidation of the chemical by singlet oxygen in the environment is evaluated from the following formula:

$$t_{\frac{1}{2}}(\mathrm{hr}) = 1.9 \times 10^{8} \times \frac{\ln(C_o/C_t)_S}{\ln(C_o/C_t)_C} \times \frac{t_C}{t_S} \times \frac{1}{k^S_{OX}} \qquad (4.2)$$

where $(C_o/C_t)_S$ or C is the ratio of concentrations of standard or chemical at times 0 and t; t_C and t_S are the times at which the concentrations of chemical and standard were taken and k^S_{OX} is the second order rate constant for reaction of singlet oxygen and standard in units of M^{-1} s^{-1}. Obviously if both components were analyzed at the same time the ratio t_C/t_S is one.

More accurate screening tests for phenols, aromatic amines, and thiols, hydroxylamines and hydrazines are needed but are not available at this time owing to complexities in the kinetic schemes for these reactions.

No detailed tests for oxidation are proposed because the most reactive and numerous classes of reactive chemicals are the phenols, amines, and hydroxylamines for which no adequate screening test is available.

A detailed test for $^1O_2$ reactions with many chemicals could be needed in some cases but more and better standard chemicals needed to be identified and tested first.

4.5.4 Scope and Limitations of Screening Tests

Screening tests for oxidation by $RO_2\cdot$ and $^1O_2$ are designed to provide the investigator approximate half-lives for chemicals in oxidation reactions to be used in comparison with half-lives for other processes. These tests are intended to be used only for chemicals which fall into one or more structural classes that are known to have relatively large rate constants for oxidation by $RO_2\cdot$ or $^1O_2$. To assist the investigator in selecting those chemicals that might be candidates for one or more oxidation screening tests we have proposed the simplified classification scheme based on structure reactivity relations discussed in Section 4.7 and shown in Schemes 2A and 2B.

4.5.5 Error Analysis

Estimation methods for error analysis of the test protocol are based on certain assumptions concerning the accuracy of specific measurements and the relationship between variables. The screening tests proposed here require only two measurements of concentration at times 0 and t. Because of the limited amount of data the error is large.

The error analysis is based on the basic kinetic rate laws cited in Section 4.7.3 and on the equations in Chapter 2 (Hydrolysis).

$$k_{OX} = \ln(C_o/C)/t$$

The estimate of the rate constant k_{OX} is related to the measured variables, concentration and time, by the following regression equation. (Statisticians often designate the estimate of k as $\hat{k}$, but we will ignore the distinction in this discussion.)

$$k_{OX} = \frac{n\Sigma t\ln C - [\Sigma t][\Sigma \ln C]}{n\Sigma t^2 - [\Sigma t]^2}$$

where C is concentration of chemical measured at time t. This version of the regression equation does not require that $\ln(C/C_o) = 0$ at $t = 0$; that is, the line is not forced through the origin and any significant departure from the origin indicates bias in values of C at $t > 0$. The preferred measure of error in experiments of this kind is the standard error, σ,* used here in the form σ^2 or the variance. The variance of k_{OX} from n measurements is given by

$$\sigma^2 = \frac{1}{n-2}\,\frac{n\Sigma[\ln C]^2 - [\Sigma \ln C]^2}{n\Sigma t^2 - (\Sigma t)^2} - (k_{OX})^2$$

This equation shows that σ varies with $\frac{1}{t}$ and $\sim\frac{1}{n}$ and directly with σ(C). If we assume that in a typical screening experiment two analyses for chemicals are performed at time = 0 and time = 5 hr with a standard percent error of 3% about the mean of 1.00×10^{-5} M, the standard percent error (σ/k) x 100 in the calculated rate constant k_{OX} is 20%.

4.6 DETAILED TESTS

No detailed tests are proposed at this time.

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[*] The standard error may be expressed as the standard deviation, (n ± σ), the error ratio, σ/k) x 100.

4.7 BACKGROUND

4.7.1 General Considerations

Oxidation is the chemical process whereby reactive electron deficient species called oxidants remove electrons from other more electron-rich molecules.* Examples of oxidants that may be found in the environment are peroxy radical ($RO_2\cdot$), hydroxy radical ($HO\cdot$), singlet oxygen ($^1O_2$), ozone (O_3), and photoexcited triplet diradicals ($\dot{R}-\dot{O}$). Oxygen ($^3O_2$) is itself rarely involved directly in reactions with stable molecules but does act as the ultimate electron sink in most environmental oxidation reactions.

This review focuses attention on reactions of the energetic oxidants found in aquatic systems, namely $RO_2\cdot$, $HO\cdot$, and $^1O_2$. We exclude from consideration here those oxidations that involve electronic excited species (singlet or triplet states) of the chemical itself (photooxidations); appropriate test methods for predictive fate assessment of photooxidations are included under the test protocol for photolysis (Section 3).

Predicting the rate of oxidation of a specific chemical in an aquatic system requires three kinds of information and data:

(1) The identities and concentrations of the oxidants in the aquatic compartment.
(2) The rate constant for oxidation by each oxidant at a specific site in a molecule.
(3) The kinetic rate law for each process.

The following sections discuss the oxidants in aquatic systems, kinetics of oxidation reactions, structure-reactivity relationships for organic molecules, and oxidation chemistry in aquatic systems. Finally the data needs for laboratory testing and predictive modeling are summarized, the kinetic basis for the proposed test procedures are formulated, and a kinetic analysis for the test methods is developed.

4.7.2 Oxidants in Aquatic Systems

For convenience in discussion we will distinguish transient oxidants such as radicals, singlet oxygen, and triplet diradicals with lifetimes of a few milliseconds from stable oxidants such as peroxides, peracids, and ozone. Our present knowledge of the transient oxidants present in natural waters is fragmentary and in some cases very qualitative. The most recent studies designed to identify and quantitate these species are summarized in Section 4.7.4. Both $HO\cdot$ and $RO_2\cdot$ radicals and $^1O_2$ have been detected by photolyzing natural waters to give products characteristic of reactions involving these oxidants (Mill et al., 1977 and Zepp et al., 1977). These oxidants must have their origin in the organic humic material present in natural waters, but the details of their photolytic generation are unknown.

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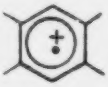
*Electron removal or transfer is often effected by simultaneous transfer of an electron and proton as $H\cdot$, namely: $X\cdot + RH \longrightarrow XH + R\cdot$.

The reactivities of important oxidants are summarized in the next section. It is worth noting that although the reactivities of $RO_2\cdot$, $^1O_2$, and $HO\cdot$ range over twelve orders of magnitude, their concentrations in aquatic systems also exhibit wide variation. As a result all of these oxidants can play important roles in some oxidation processes. Further research may show that alkoxy radicals ($RO\cdot$) and diradicals also contribute to some oxidation processes, but their contributions are now incorporated as part of the calculated concentration of $RO_2\cdot$, which, although much less reactive, undergoes similar reactions. Still other transient oxidants peculiar to aquatic systems may include superoxide anion ($\cdot O_2^-$), ferrate ion ($HOFe^{4+}$), and polyaromatic radical cations



The presence of these species in water, however, is entirely speculative.

Stable oxidants have been detected in natural waters, but they have not been identified (see Section 4.7.4). Very likely several peroxides including hydrogen peroxide (H_2O_2,) alkyl hydroperoxides (ROOH) and peracids [RC(O)OOH) are formed by oxidation of natural organic structures, but speciation of these peroxides has not been accomplished and their actual importance in environmental oxidation is questionable. Rate constants for their reactions with reactive organic structures generally are smaller by two to twelve orders of magnitude than for reactions with $RO_2\cdot$, $HO\cdot$ or $^1O_2$ [Corci and Edwards (1970) and Swern (1970)].

4.7.3 Oxidation Chemistry and Kinetics

General Considerations

The simplest form of the oxidation rate law is

$$R_{OX} = k_{OX}[C][OX] \qquad (4.3)$$

where k_{OX} is the specific second order rate constant for oxidation at a specific temperature and [C] and [OX] are molar concentrations of chemical and oxidant respectively; k_{OX} is usually given in units of $M^{-1}\ s^{-1}$. The total rate of oxidation of a chemical is the sum of the rates for reaction of each kind of oxidant with C:

$$R_{OX(T)} = (k_{OX_1}[OX_1] .. + k_{OX_n}[OX_n])[C] \qquad (4.4)$$

$$= [C]\Sigma k_{OX_n}[OX_n]$$

The simplest way to use equation (4.4) is to assume that the concentration of each oxidant, OX_n, is constant during the measurement interval, in which case the equation simplifies to a pseudo-first-order form

$$R_{OX}(t) = \Sigma k'_{OX_n}[C] \qquad (k'_{OX_n} = k_{OX_n}[OX_n]) \tag{4.5}$$

Integration between the time limits o and t gives

$$\ln([C_o]/[C_t]) = \Sigma k'_{OX_n}t \tag{4.6}$$

and

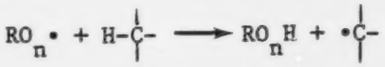
$$t_{\frac{1}{2}} = 0.693/\Sigma k'_{OX_n} \tag{4.7}$$

We can use equations (4.6) and (4.7) to estimate the persistence of a chemical in an aquatic environment only if we can identify the oxidants and evaluate their rate constants. The next two sections discuss briefly the chemistry of HO•, RO_2•, and $^1O_2$, oxidants found in aquatic systems, and values of rate constants for their reactions with organic chemicals.

Radical Oxidants RO_2•, RO_2, and HO•

Most radical oxidants exhibit similar chemistry for aliphatic organic structures, but depart significantly in their reactions toward aromatics and heterocycles. Extensive reviews of oxidation chemistry are found in (Walling, 1957; Howard, 1972; Ingold, 1969; and Mayo, 1968). Four common processes are known

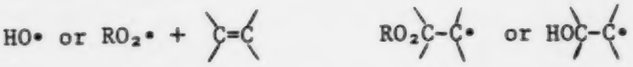
(1) H-atom transfer



$$RO_n\bullet + H-\overset{|}{\underset{|}{C}}- \longrightarrow RO_nH + \bullet\overset{|}{\underset{|}{C}}- \qquad (n = 1 \text{ or } 2)$$

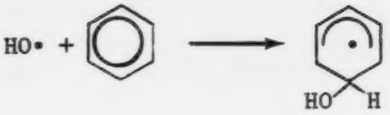
R = alkyl or H; n = 1 or 2

(2) Addition to double bonds



R = alkyl or H

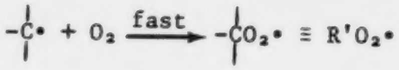
(3) HO• addition to aromatics



(4) RO_2• transfer of O-atoms to certain nucleophilic species

$$RO_2\cdot + PR_3' \longrightarrow RO\cdot + OPR_3$$

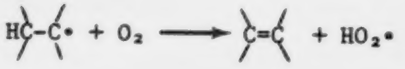
The fate of carbon radicals formed by H-atom transfer is to add oxygen to form new $RO_2\cdot$ and then either chain transfer with other molecules or terminate by reactions with other radicals

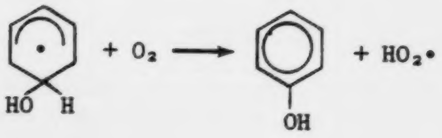
 (4.8)

$$-\overset{|}{\underset{|}{C}}\cdot + O_2 \xrightarrow{\text{fast}} -\overset{|}{\underset{|}{C}}O_2\cdot \equiv R'O_2\cdot \qquad (4.8)$$

$$R'O_2\cdot + RO_2\cdot \longrightarrow \text{stable products} + O_2 \qquad (4.9)$$

Some carbon radicals including cyclohexadienyl radical react by 1,2 or 1,4-elimination to give olefins or substituted aromatic rings and $HO_2\cdot$

 (4.10)

 (4.11)

The rate law for radical oxidation in aquatic systems is readily formulated as the sum of two bimolecular expressions

$$R_{OX} = k_{RO_2}[C][RO_2\cdot] + k_{HO}[C][HO\cdot] \qquad (4.12)$$

Although many different kinds of alkylperoxy radicals could be present in a natural system, we can make a simplifying assumption that the structure of R in $RO_2\cdot$ (primary, secondary, or tertiary) has little effect on its reactivity (a reasonable assumption within a factor of ten); we can then use a lumped rate constant k_{RO_2} and use $[RO_2\cdot]$ to represent the total concentration of these radicals [equation (4.8)]. A large number of rate constants k_{RO_2} and k_{HO} are known for organic chemicals (Howard, 1972; Hendry, 1974; and Denisov, 1971). Concentrations of $RO_2\cdot$ and $HO\cdot$ in aquatic systems have been estimated from studies of Mill et al. (1977). With these values and equation (4.12) we can estimate half-lives for different chemicals in reactions with these oxidants at environmentally realistic concentrations. Tables 4.1 through 4.3 summarize these values and include data for $RO\cdot$ radical at 10^{-14} M.

Two important conclusions emerge from inspection of the data in these tables. First, the range of reactivity of $HO\cdot$ toward most organic structures is much smaller, (a factor of 100 at most) than for $RO_2\cdot$ even though the absolute reactivity of $HO\cdot$ is 5 to 10 orders of magnitude greater than for $RO_2\cdot$.

TABLE 4.1. RATES OF OXIDATION BY $RO_2\cdot$ RADICAL

Class	k_p M^{-1} s^{-1}	Half-Life, $t_{½}$[a] (days)
Olefin	0.09	9×10^4
Benzyl	1	8×10^3
Aldehyde	0.1	8×10^4
Alcohol	0.01	8×10^5
Phenol	1×10^4	0.8
Aromatic amine	1×10^4	0.8
Hydroquinone	1×10^6	12 min
Hydroxylamine	1×10^5	120 min
Hydroperoxide	1×10^5	120 min
Polycyclic aromatic	1×10^3	8

[a] For 10^{-9} M $RO_2\cdot$

TABLE 4.2. RATES OF OXIDATION BY $RO\cdot$ RADICAL

Class	$k_A \times 10^{-5}$ M^{-1} s^{-1}	Half-Life, $t_{½}$[a]
Alkane	0.3	73 year
Olefin	24	334 days
Benzyl	10	801 days
Alcohol	1	22 year
Aromatic amine	3000	64 hour
Phenol	1000	192 hour

[a] For 10^{-14} M $RO\cdot$

TABLE 4.3. RATES OF OXIDATION BY HO• RADICAL

Class	$k_{HO} \times 10^{-9}$ $M^{-1}\ s^{-1}$	Half-life $t_{1/2}$ (days)[a]
Alcohols	1	800
Ethers	2	400
Ketones	0.9 - 2.0	400 - 900
Aromatics	1 - 5	800-160
Olefins	0.5 - 2	400 - 1600
Dienes	10	80
Hydroquinones	12	67

[a] For 10^{-17} M HO•

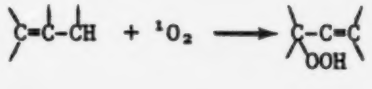
Second, because the concentration of HO• estimated in aquatic systems is low, HO• is of negligible importance as an oxidant for most types of organic structures, whereas RO_2• can be important for certain classes of common but reactive organic structures.

The reactivity and selectivity of RO• (or triplet diradical $\dot{R}\text{-}\dot{O}$) falls somewhere in between those of RO_2• and HO•; the possible importance of RO• as an environmental oxidant remains uncertain until some evidence can be found for its presence or absence in aquatic systems.

Singlet Oxygen ($^1O_2$)

Singlet oxygen ($^1O_2$), is an electronically excited form of oxygen which has 22 kcal/mol more energy than its triplet ground state form,* is very electrophilic, and exhibits a wide variety of reactions with organic structures not observed with triplet oxygen. These reaction, though diverse, can be categorized as five types (Foote, 1976).

(1) Ene-reaction with many internal olefins to give allylic hydroperoxides



(4.13)

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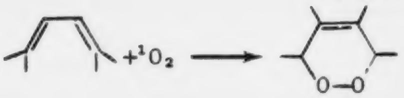
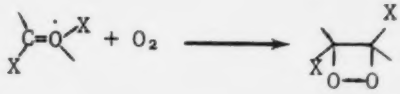
[*] A higher energy form ($^1\Sigma_g^+$, 37 kcal) is not important in photooxidation chemistry (Kearns, 1970).

(2) Cyclo addition to dienes (2 + 4)



(4.14)

(3) Cycloaddition to electron rich olefins (2 + 2)



(4.15)

(4) Oxidation of sulfur in sulfides, disulfides, and mercaptans

$$2R_2S + {}^1O_2 \longrightarrow 2R_2SO \qquad (4.16)$$

(5) Electron transfer from phenols and other electron donors

$$ArOH + {}^1O_2 \longrightarrow ArO\bullet + HO_2\bullet \qquad (4.17)$$

Rate constants for these processes generally range from 10^4-10^7 M^{-1} s^{-1}. Table 4.4 summarizes rate constants for reactions of several types of organic structures with $^1O_2$ and lists half-lives based on the recent estimate of Zepp et al. (1977) for the concentration of $^1O_2$ in aquatic systems.

Singlet oxygen, like $RO_2\bullet$, exhibits a very wide range of reactivity toward organic structures. Table 4.4 shows that, at the concentrations reported in aquatic systems ($\sim 10^{-12}$ M), its reactions with certain classes of organic structures can be important loss processes. For this reason screening tests for oxidation by $^1O_2$ are recommended for selected classes of chemicals.

TABLE 4.4. RATES OF OXIDATION BY SINGLET OXYGEN

Structure	k^1O_2 $M^{-1}\ s^{-1}$	$t_{1/2}$[a]
Unsubstituted olefin	3×10^3	7.3 day
Cyclic olefins	2×10^5	40 day
Substituted olefin	1×10^6	8.0 day
Dialkyl sulfide	7×10^6	27 hr
Diene	1×10^7	19 hr
Imidazole	4×10^7	4.8 hr
Furan	1.4×10^8	1.0 hr
Trialkyleneamine	3×10^8	14 min

[a] For 10^{-12} M $^1O_2$; see section 4.7.4.

Measurement of k_{RO_2} for $RO_2\cdot$ Oxidations

The kinetics of oxidation involving H-atom transfer from CH bonds is described by the following scheme where RH is any CH bond:

Initiation	$\text{Initiator} \xrightarrow{k_i} 2X\cdot$	(R_i)	(4.18)
	$X\cdot + RH \longrightarrow XH + R\cdot$		(4.19)
	$R\cdot + O_2 \longrightarrow RO_2\cdot$		(4.8)
Propagation by $RO_2\cdot$	$RO_2\cdot + RH \longrightarrow RO_2H + R\cdot$	(k_{RO_2})	(4.20)
	$2RO_2\cdot \longrightarrow 2RO\cdot + O_2$	(ak_x)	(4.21)
Propagation by $RO\cdot$	$RO\cdot + RH \longrightarrow ROH + R\cdot$	(k_{RO})	(4.22)
Termination	$2RO_2\cdot \xrightarrow{k_t} \text{Products}$	$[(1-a)k_x = k_t)$	(4.23)

Reactions (4.8) through (4.18) may be used to derive several important relationships. Oxygen consumption is expressed as

$$-\frac{dO_2}{dt} = R_{O_2} = k_{RO_2}[RH][RO_2\bullet] + k_{RO}[RH][RO\bullet] \qquad (4.24)$$

$$R_{O_2} = \left(\frac{R_i}{2k_t}\right)^{1/2} k_{RO_2}[RH] + \frac{R_i}{a} \qquad (4.25)$$

where R_i is the rate of radical formation ($R_i = 2k_d$[Initiator] and the R_i/a term takes into account oxidation by RO• radicals and initiators. R_i can be controlled by using an added free radical source.

If RO• cleaves to form new carbon radicals, termination becomes more complex, involving two different $RO_2\bullet$ in three possible termination reactions. However, if enough RO_2H is added to the reaction to scavenge all RO•

$$RO\bullet + RO_2H \longrightarrow ROH + RO_2\bullet \qquad (4.26)$$

the rate law for oxidation simplifies to

$$R_{O_2} = \left(\frac{R_i}{2k_t}\right)^{1/2} k_{RO_2}[RH] \qquad (4.27)$$

This equation can be used to evaluate k_{RO_2} from oxygen uptake if k_t and R_i are known. Usually, however, both k_{RO_2} and k_t for a new chemical are unknown and some other method must be sought to measure k_{RO_2}. The simplest method is to add 0.2- 1.0 M $t\text{-}BuO_2H$ to the solution of the chemical so that all $RO_2\bullet$ are efficiently converted to $t\text{-}BuO_2\bullet$

$$RO_2\bullet + t\text{-}BuO_2H \longrightarrow RO_2H + t\text{-}BuO_2\bullet \qquad (4.28)$$

Now all propagation and termination reactions occur by way of $t\text{-}BuO_2\bullet$, for which the value of $2k_t$ is known with considerable accuracy at 30°-100°C (Howard and Ingold, 1968)

$$X\bullet + RH \longrightarrow XH + R\bullet \qquad (4.29)$$

$$R\bullet + O_2 \longrightarrow RO_2\bullet \qquad (4.8)$$

$$RO_2\bullet + t\text{-}BuO_2H \longrightarrow RO_2H + t\text{-}BuO_2\bullet \qquad (4.30)$$

$$t\text{-}BuO_2\bullet + RH \longrightarrow t\text{-}BuO_2H + R\bullet \qquad (4.31)$$

$$2\text{-}t\text{-}BuO_2\bullet \longrightarrow 2\text{-}\ t\text{-}BuO\bullet + O_2 \qquad (4.32)$$

$$t\text{-}BuO\bullet + t\text{-}BuO_2H \longrightarrow t\text{-}BuOH + t\text{-}BuO_2\bullet \qquad (4.33)$$

$$R_{O_2} = \left[\frac{R_i}{2k_{t(t-BuO_2)}}\right]^{1/2} k_{p(t-BuO_2)}[RH] \qquad (4.34)$$

$$k_{p(t-BuO_2)} = R_{O_2}[2k_{t(t-BuO_2)}]^{1/2}/R_i^{1/2}[RH] \qquad (4.35)$$

$k_{p-(tBuO_2)}$ is the specific rate constant for H-atom transfer from RH to $t\text{-}BuO_2\cdot$; its value will be similar to values for other k_{RO_2}. This method for evaluating k_{RO_2} has been used extensively (Howard, 1972) and is the method of choice in cases where there is no direct reaction between $t\text{-}BuO_2H$ and the chemical.

The method can be further simplified by using a standard chemical (SH) for which k_{t-BuO_2} has been carefully measured by the above method or by an absolute method. In this case at low conversions of standard SH and unknown RH where their concentrations change very little ($k_{t-BuO_2} \equiv k_{RO_2}$)

$$\frac{\Delta[CH]}{\Delta[RH]} = \frac{k_{RO_2(SH)}[t\text{-}BuO_2\bullet][SH]}{k_{RO_2(RH)}[t\text{-}BuO_2\bullet][RH]} = \frac{k_{RO_2(SH)}[SH]_{av}}{k_{RO_2(RH)}[RH]_{av}} \qquad (4.36)$$

Since both Δ[SH] and Δ[RH] are very small, their values are inaccurately determined by measuring their concentrations at times o and t; they are very accurately determined by measuring [SOOH] and [ROOH] at time t.

$$\frac{\Delta[SH]}{\Delta[RH]} = \frac{[SOOH]}{[ROOH]} = \frac{k_{RO_2(SH)}[CH]_{av}}{k_{RO_2(RH)}[RH]_{av}} \qquad (4.37)$$

Furthermore, the difficult direct analyses for SOOH and ROOH may be avoided by reducing the mixture with $NaBH_4$ (in water) or $(C_6H_5)_3P$ (in organic solvent) to the mixture of corresponding alcohols and analyzing for their ratio.

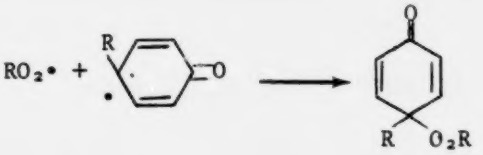
The expression for the unknown value of $k_{RO_2(RH)}$ is then

$$k_{RO_2} = k_{RO_2}(SH)\frac{[SH]}{[RH]_{av}} \times \frac{[SOH]}{[ROH]} \qquad (4.38)$$

If more than one type of CH bond in RH is oxidized, which is usually the case, then the ratio of isomeric ROH gives values for k_{RO_2} for each different CH bond. This method is applicable to a broad group of chemicals that oxidize via CH-atom transfer or addition to a double bond. This group includes most alkanes, olefins, ethers, alkyl halides, and similar structures. However, table 4.1 shows that oxidations of CH bonds are generally very slow under environmental conditions: even the most reactive of dienes, cyclohexadiene with $k_p \sim 300\ M^{-1}\ s^{-1}$, has a half-life of 641 hours (26 days) in reactions with 10^{-9} M $RO_2\bullet$, the concentration reported in some natural waters. Most types of oxidations of CH bonds are far slower (Hendry et al., 1974).

The most reactive chemicals in oxidation with t-$RO_2\bullet$ are those in which H-atom transfer occurs from O, N, or S (see Table 4.1) and where no $RO_2\bullet$ chain is possible; termination reactions between $RO_2\bullet$ and, for example, $ArO\bullet$ are very rapid

$$RO_2\bullet + ArOH \longrightarrow RO_2H + ArO\bullet \qquad (4.39)$$



(4.40)

Many phenols, aromatic amines, and thiols are effective inhibitors for this reasons.

Oxidations of these chemicals are often complex and involve competitive terminations between $RO_2\bullet$ and $ArO\bullet$ (or ArNH). Moreover the back reaction of $ArO\bullet + RO_2H$ is usually rapid.

Step 1: $RO_2\bullet + ArOH \longrightarrow RO_2H + ArO\bullet$ (k_1) (4.41)

Step 2: $ArO\bullet + RO_2H \longrightarrow ArOH + RO_2\bullet$ (k_2) (4.42)

Step 3: $2ArO\bullet \longrightarrow$ coupling products (k_3) (4.43)

Step 4: $ArO\bullet + RO_2\bullet \longrightarrow RO_2ArO$ (k_4) (4.44)

Step 5: $2RO_2\bullet \longrightarrow R_2O_2 + O_2$ $(2k_t)$ (4.45)

Rate constants for the steps in this sequence are known for many phenols and some amines and thiols. Typically k_1 or k_2 is 10^4, and k_{-1} or k_{-3} is 10^3 M^{-1} s^{-1}; steps 3 or 4 have rate constants of 10^7 M^{-1} s^{-1} (Mahoney and DaRooge, 1975) much faster than step 5 for which $2k_t \sim 10^3$ M^{-1} s^{-1} (Howard et al., 1972).

Kinetics of inhibition, which basically involve a competition for $RO_2\bullet$ between a phenolic or amine inhibitor and a hydrocarbon, (RH), can be complex owing to varying combinations of the reactions in steps 1 through 5 and

Step 6: $RO_2\bullet + RH \longrightarrow RO_2H + RO_2\bullet$ (4.46)

But in the simplest case where only steps 1, 4, and 6 are important, the rate law takes the form

$$-\frac{dO_2}{dt} = -\frac{d[RH]}{dt} = R_{O_2} = R_i k_6[RH]/nk_1[ArOH] \qquad (4.47)$$

where n is the number of $RO_2\bullet$ that react with each ArOH (usually 2). Equation (4.47) can be used to evaluate k_1 by measuring oxygen uptake or loss of RH as a function of the ratio [RA]/[ArOH]. However, equation (4.47) can be used only if the system is shown by kinetic analysis to follow this simple relationship, hardly a routine procedure suitable for standard test methods.

The use of added hydroperoxide to simplify the kinetics of oxidations at CH bonds is not applicable to oxidation of OH or NH bonds because of the rapid reaction of ArO• or ArNH with t-BuO_2H (Step 2) and the possible direct reaction of some phenols and amines with hydroperoxide (Hiatt, 1970).

An approximate estimate of k_1 may be obtained by measuring the loss of ArOH in the presence of $RO_2\bullet$, where the ratio $[AH]/[RO_2\bullet] < 1$. Under these conditions, the bulk of $RO_2\bullet$ will terminate by self-reactions and the kinetic expression

$$d[ArOH]/dt = (R_i/2k_t)^{1/2} k_1 [ArOH] \qquad (4.48)$$

applies. To achieve the low ratio $[ArOH]/[RO_2\bullet]$ needed for application of this equation, a large concentration of initiator and low concentration of ArOH are needed, a requirement that imposes unreasonable limitations on the test procedure. Therefore, the recommended screening test procedure is carried out under conditions that provide only a lower limit for k_1 for these reactive chemicals.

Preliminary computer modeling of the reaction of $RO_2\bullet$ and a phenol indicates that at 50°C if k_1 is larger than $1 \times 10^4\ M^{-1}\ s^{-1}$, the rate of loss of phenol will nearly equal one-half the rate of production of $RO_2\bullet$. Under this condition all $RO_2\bullet$ are scavenged by the phenol and the rate of loss of phenol is zero order.

$$\text{Initiator} \longrightarrow 2RO_2\bullet \qquad R_i = 2k_d[MAB] \qquad (4.49)$$

$$RO_2\bullet + ArOH \longrightarrow RO_2H + ArO\bullet \qquad (4.41)$$

$$RO_2\bullet + ArO\bullet \longrightarrow RO_2ArO \qquad (4.44)$$

$$d[ArOH]/dt = k_1[RO_2\bullet][ArOH] \qquad (4.50)$$

$$[RO_2\bullet] = R_i/2k_1[ArOH] \qquad (4.51)$$

$$d[ArOH]/dt = R_i/2 \qquad (4.52)$$

Measurement of k_{OX} for $^1O_2$ Oxidations

Kinetic schemes for $^1O_2$ oxidations can be written in the general form (Foote, 1968),

$$Sen \xrightarrow{h\nu} Sen^*$$

$$Sen^* + O_2 \longrightarrow Sen + {}^1O_2 \qquad (\phi k_T) \qquad (4.53)$$

$${}^1O_2 + C \longrightarrow CO_2 \qquad (k_{OX}) \qquad (4.54)$$

$${}^1O_2 + S \longrightarrow S + O_2 \text{ or } SO_2 \ (k_S) \qquad (4.55)$$

$$^1O_2 \longrightarrow {}^3O_2 \qquad (k_d) \qquad (4.56)$$

Where Sen* is a triplet sensitizer (usually a dye), C is the chemical of interest; S is a chemical that competes at a known rate with the test chemical, C, for $'O_2$, and k_d is the rate of the radiationless transition from singlet to ground state. Of interest here is the value of k_{OX} where k_S and k_d are known. Merkel and Kearns (1972) measured k_{OX} directly using a pulsed laser technique in which the loss of the chemical (diphenylisobenzofuran) was measured spectrometrically following pulse irradiation of methylene blue sensitizer in methanol. The rate law

$$-2.31\log([C] - [C]_\infty) = (k_d + k_{OX}[C])t \qquad (4.57)$$

was used to evaluate k_{OX}, at nearly constant [C],

Young et al. (1971) described a general competitive technique to evaluate relative rate constants in which the loss of standard chemical is followed at different initial concentrations of chemical

$$d[S]/dt = \frac{\phi k_T k_S[C]}{k_S[S] + k_{OX}[C] + k_d} \qquad (4.58)$$

If k_S [S] is made small compared with other terms in the denominator, by keeping [S] below $< 10^{-6}$ M, then the equation simplifies

$$\frac{d[C]}{dt} = \frac{\phi k_T k_S[S]}{k_{OX}[C] + k_d} \qquad (4.59)$$

Experiments were run at different initial concentrations of C and, with only small changes in C, the loss of S follows the first-order relation

$$\ln(S_o/S) = \phi k_T k_S/k_{OX}[C] + k_d \qquad (4.60)$$

The ratio of slopes ($s\ell$) in two or more experiments, one of which ($s\ell_o$) has no C is

$$(s\ell_o/s\ell_c) = 1 + k_{OX}[C]/k_d \qquad (4.61)$$

A plot of $(s\ell_o/s\ell_c)$ versus [C] gives the ratio k_{OX}/k_d from which k_{OX} is readily estimated since k_d in most solvents is known reasonably well (Foote, 1976).

Recently Kraljic et al. (1977) investigated the rate of oxidation of allythiourea (ATU) in water and measured k_{OX} using a competitive water soluble physical quencher, azide ion (N_3^-). Their kinetic relation is based on initial oxygen uptake at different ratios of ATU and N_3^-.

$$\frac{1}{\Delta O_2} = \frac{1}{k_T\phi}[1 + (k_3[C]/k_{OX}[ATU])] \qquad (4.62)$$

The value of k_S is 2×10^8 M^{-1} s^{-1} and from the measured ratio of rate constants k_{OX} is 4×10^6 M^{-1} s^{-1} for ATU.

Foote and Denny (1968) used a similar inhibition kinetics analysis to evaluate the quenching rate constant for carotene in MeOH:C_6H_6

$$\frac{1}{CO_2} = \left(\frac{1}{\phi k_T}\right)[1 + \left(\frac{k_d}{k_C} + \frac{k_{OX}[C]}{k_S}\right)\frac{1}{[S]}] \qquad (4.63)$$

In this case C was 2-methyl-2-pentene. A plot of $[CO_2]^{-1}$ versus $[C]^{-1}$ with varying amounts of S gives a series of straight lines from which they evaluated first k at [C] = 0 and then k_{OX}/k_S. As a further check, they plotted $[CO_2]^{-1}$ versus [S] at constant [C] to evaluate the same ratio k_{OX}/k_S.

Simple competitive techniques also have been used for estimating relative reactivity toward $^1O_2$. Bartlett et al. (1970) evaluated the relative rate constants for a series of vinyl ethers in acetone. Gollnick et al. (1970) measured reactivities for a series of olefins and Matsura et al. (1973) measured relative reactivities for cyclic olefins in methanol. Relative reactivities are expressed as the ratio of two first-order processes

$$\frac{\ln(C_o/C)_A}{\ln(C_o/C)_B} = \frac{k_{OX}(A)}{k_{OX}(B)} \qquad (4.64)$$

where A and B refer to two different chemicals. This method has great advantages of simplicity over inhibition kinetic methods, but does require more careful analyses for loss of chemical and selection of a standard that has a reactivity similar to that of the test chemical. Some trial and error measurements may be necessary with many chemicals, although the general rule that similar structures will have similar reactivities is a useful guide for selection of reference chemicals. The use of a standard chemical will also help detect test chemicals, such as azide ion, diazabicyclooctane, and carotene, that are not only unreactive toward $^1O_2$ but also rapidly quench the oxidant by a physical process.

β Values

The ratio k_d/k_{OX} (or k_d/k_S) is called β, the value of which equals the concentration of chemical needed to trap half the $^1O_2$. β values in water range from > 8 M for unreactive olefins to ∿ 1×10^{-3} for reactive furans and polycyclic aromatics. The value of k_d, but not k_{OX}, is markedly dependent on solvent: in organic solvents k_d is ∿ 10^5 s^{-1}; in H_2O, k_d ∿ 10^6 s^{-1}. k_d decreases almost tenfold when D_2O is substituted for H_2O , evidently because conversion of $^1O_2$ to $^3O_2$ requires close matching of energy levels between $^1O_2$ and H-O or D-O bonds (Merkel and Kearns, 1972).

Water, therefore, offers special problems to the investigator because at the short lifetime of $^1O_2$ and the low solubility of many chemicals in water. At a concentration of 10^{-5} M, even the most reactive chemical will trap only 1% of the available $'O_2$, leading to slow oxidation.

Solvent Effects on Oxidation Reactions

Although the screening tests for evaluating reactivities of chemicals in oxidations are used in water or water with acetonitrile because of the obvious relevance for environmental assessment, it is useful to consider what effect solvent properties have on reactivity because many rate constants and products of oxidations have been measured in organic solvents and few have actually been measured in water. Values of k_{OX} in nonaqueous systems may be useful for screening purposes.

Radical Oxidants. The bulk of evidence points to only small solvent effects on reactions of $RO_2\bullet$ with CH bonds (Howard, 1972) as expected for reactions that have little true ionic character in either the ground or transition states. However, direct reaction of $RO_2\bullet$ or $t\text{-}BuO_2\bullet$ with many organic solvents may be competitive with reaction with the test chemical if it is present in much smaller concentration. Reactions of $RO_2\bullet$ with heteroatom-H bonds such as with phenols or amines might be expected to exhibit solvent effects in water associated with competitive hydrogen bonding of the chemical to water and to $RO_2\bullet$. Kinetic evidence indicates that H-atom transfer from phenols to $RO_2\bullet$ proceeds via an intermediate complex, possibly involving a quasi H-bond (Howard and Furimski, 1973)

$$RO_2\bullet + HOAr \rightleftharpoons R\dot{O}_2\ldots HOAr \qquad (4.65)$$

$$RO_2\ldots HOAr \longrightarrow RO_2H + \bullet OAr \qquad (4.66)$$

Competition with the water-bonded form of phenol

$$ArOH\ldots OH_2 \rightleftharpoons ArOH + H_2O\ (K_1) \qquad (4.67)$$

would reduce the effective concentration of ArOH available to $RO_2\bullet$ and lower the value of the observed second-order rate constant.

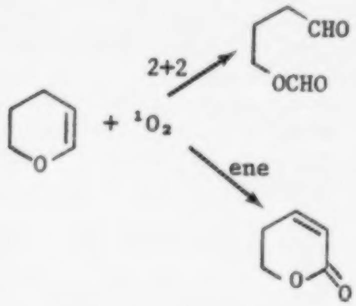
$$\text{Rate} = k_{obs}K_1[ArOHOH_2] \qquad (4.68)$$

Few data are available to indicate the extent of this possible effect, but preliminary data on p-cresol oxidation by $RO_2\bullet$ in water (Mill and Baraze, 1978) indicate that it is less than a factor of ten.

Singlet Oxygen. Solvent effects on rates of reactions of singlet oxygen ($^1O_2$) have been investigated in detail (Merkel and Kearns, 1972; Foote et al., 1972; Young et al., 1971). Absolute rate measurements of Merkel and Kearns (1972) show clearly that solvent affects mostly the value of k_d, the unimolecular rate constant for radiationless decay to ground-state triplet oxygen. In water k_d is larger than in any other solvent and the lifetime ($1/k_d$), is the shortest (2μsec). In CS_2 and CCl_4, k_d is much smaller and $1/k_d$ is 200-700 μsec. These investigators also showed that deuteration of water or methanol increased the lifetime of $^1O_2$ almost tenfold; deuteration of acetone, however, had little effect on lifetime. Evidently, the transition involves coupling of electronic to vibrational levels in H-O bonds. This observation is the basis for the use of D_2O or CD_3OD to confirm the role of $^1O_2$, rather than some other oxidant, in a photooxygenation process (see, for example, Zepp et al., 1977).

Solvent appears to have little effect on the rate of reaction of $^1O_2$ with some classes of chemicals. The rate of reaction of diphenylisobenzofuran was unchanged in several solvents (excluding water) where dimerization may have accelerated its reactivity (Merkel and Kearns, 1972). However, Young et al. (1971) noted that $^1O_2$ oxidation of some furans showed significant solvent effects (x32), whereas reactions with olefins showed only small effects (< x2).

Products of $^1O_2$ reactions with some olefins show striking solvent effects on the partition between the ene and 2+2 addition (Bartlett and Schaap, 1970)



polar solvent (4.69)
(CH_3CN)

nonpolar solvent (4.70)
(C_6H_6)

In water we would expect reactions of this kind would proceed mostly (> 90%) by the 2+2 route, but we know of no specific examples. The effect of solvent properties mainly on product composition and less on rate points to the possibility of doing rate studies in mixed solvents with water, but the necessity of doing product studies in water alone or water containing only a small amount of acetonitrile.

Temperature Effects in Oxidation

The review of H-atom transfers by $RO_2\cdot$ from CH bonds (Hendry et al., 1974) indicates that activation energies for these processes range from 9 to 18 kcal/mol. Activation energies for oxidation of only the most reactive CH bonds ($k_p > 100\ M^{-1}\ s^{-1}$) are close to 10 kcal/mol, corresponding to a factor of 3.7 in rate between 25° and 50°C. H-atom transfers from OH or NH bonds to $RO_2\cdot$ in organic solvents have much smaller activation energies, close to 1 kcal/mol (Howard and Furimsky, 1973), corresponding to only a 10% change in rate between 25° and 50°C. In effect, these latter oxidations are temperature-independent in the temperature range of environmental concern. Special solvent effects in water might increase these activation energies by the heat of reaction of hydrogen bonding of phenols or amines to water.

Singlet oxygen reactions have less well-characterized temperature dependences. However, two lines of evidence indicate that the activation energies must be quite low: (1) reactions are often carried out at -25° to -70°C and proceed quite rapidly; and (2) if the activation entropies have normal bimolecular values ($\sim 10^9\ M^{-1}\ s^{-1}$), (Benson, 1976) then activation energies must be less than 2 kcal/mol for the most reactive chemicals (10^8 M^{-1} s^{-1}) corresponding to less than a 30% change in rate between 25° and 50°C. For less reactive chemicals ($k \sim 10^5$ M^{-1} s^{-1}), activation energies are still less than 6 kcal/mol, a factor of 2.2 over the same temperature range. The generally small activation energies for oxidation by $RO_2\cdot$ and $^1O_2$ simplify the requirements for temperature control in test methods and for the need to correct measured values back to 25°C except for the case of $RO_2\cdot$ oxidations of CH bonds.

4.7.4 Review of Environmental Oxidation Studies

General

Photooxidation under environmental conditions occurs with a wide variety of chemicals as evidenced by the need for oxygen and/or by isolation of oxidation products under sterile conditions. In only a few cases, however, have these processes been shown to involve oxidation by thermal oxidants such as free radicals rather than by direct photolysis. A good illustration of the distinction between photooxidation involving excited state chemistry and oxidation involving thermal oxidants is found by comparing the reports of Crosby and Tang (1969) and Crosby and Wong (1973) on the direct photolyses of naphthalene acetic and chlorophenoxy acetic acid salts with the reports of Crosby and coworkers on photooxidations of aldrin, carbamates and Mill et al. (1977) on the oxidation of cumene, which occur in natural waters but not in pure water.

Direct photolysis of phenoxyacetic or naphthalene acetic acid salts above 300 nm gives mixtures of products that probably form from radical intermediates generated by electron transfer from the acid salt excited states

$$ArCH_2CO_2^- \xrightarrow{h\nu} \overset{*}{ArCH_2CO_2^-} \qquad (4.71)$$

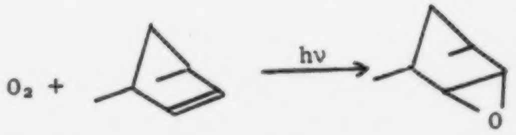
$$\overset{*}{ArCH_2CH_2^-} + O_2 \longrightarrow ArCH_2CO_2\cdot + \cdot O_2^- \qquad (4.72)$$

$$ArCH_2CO_2\cdot \longrightarrow ArCH_2\cdot + CO_2 \qquad (4.73)$$

$$ArCH_2\cdot + O_2 \xrightarrow[\text{steps}]{\text{several}} (ArCH_2OH) \longrightarrow Ar\cdot + CH_2O \qquad (4.74)$$

Ar = napthyl or chlorophenoxyl

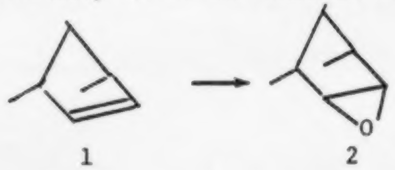
The photochemical conversion of aldrin (1) to dieldrin (2) (Ross and Crosby, 1975)



(4.75)

is not observed in pure water (aldrin does not absorb light in the solar region); however, photolysis of solutions of aldrin in pure water containing acetone or in natural water from rice paddys leads to rapid loss of aldrin and formation of varying amounts of dieldrin. Experiments using singlet oxygen showed that it was not the effective oxidant. Peracids were found to effect the oxidation of 1 to 2, but the concentration required to achieve the rates observed are far too high to make peracid the likely oxidant. We believe that either $RO_2\cdot$ or $RC(O)O_2\cdot$ is more likely to be the oxidant in this system.

$RO_2\cdot$ or $RC(O)O_2\cdot$ +



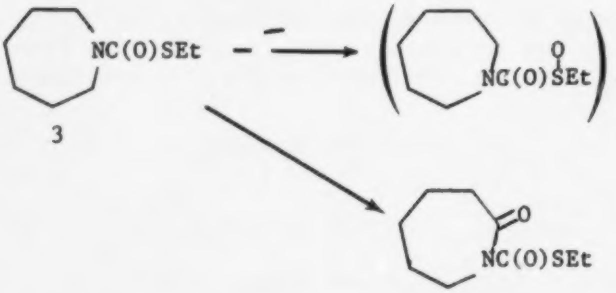
1

2

+ $RO\cdot$ or $RC(O)O\cdot$ (4.76)

Ethylene thiorea is also reported to undergo oxidation in natural water, but not in pure water, to give ethylene urea and glycine sulfate, again suggesting that radical oxidants or singlet oxygen are involved.

More recent studies by Crosby and coworkers have shown that oxidation can account for partial losses of several important agricultural chemicals and that stable oxidants are formed in natural waters. Molinate (3) appears to oxidize by two mechanisms (Soderquist and Crosby, 1976)



3

(4.77)

(4.78)

A free radical oxidation seems likely to account at least for oxidation in the ring while oxidation at sulfur may be radical or singlet oxygen in origin.

Another thiolcarbamate, benzthiocarb (4), oxidizes on photolyses in natural water to products also found when 4 was oxidized with $HO\cdot$ radical (Crosby and Draper, 1978). They noted that other rice pesticides also oxidized readily under these conditions and inferred that $HO\cdot$ radical may be an important oxidant in natural waters

$$\underset{4}{4\text{-}ClPhCH_2SC(O)NEt_2} \xrightarrow{h\nu} Cl,HOPhCH_2SC(O)NEt_2 + ClPhCH_2S(O)C(O)NEt_2 \qquad (4.79)$$

Draper and Crosby (1976) reported that sunlight irradiation of several kinds of natural waters leads to measurable concentrations of oxidants capable of oxidizing leucocrystal violet to the colored form. In terms of H_2O_2 equivalents, samples of irradiated water formed 1 to 24 $\mu\underline{M}$ oxidant on exposure for 200 minutes; the average value was close to 2 μM with a sewage stream having the high value and seawater the low value.

The foregoing reactions are cited as examples of photolytic processes that have the earmarks of chemical oxidations but for which no incisive evidence has been adduced as to the oxidants(s) involved. The following sections summarize recent work that attempts to identify the oxidants formed in natural water on irradiation with sunlight or light in the solar region.

Radical Oxidants

Mill et al. (1977) investigated the role of free radicals in environmental processes by first measuring the kinetics and products of radical oxidation of selected molecules toward $RO_2\bullet$ and $RO\bullet$ in pure water and then measuring rates and products in natural waters exposed to sunlight. Cumene (isopropylbenzene, CuH) was used as the principal probe for free radicals because it reacts with $RO_2\bullet$ and $HO\bullet$ but is not reactive toward $^1O_2$ and does not photolyze in sunlight in pure water. However, photolysis of cumene in natural waters leads to formation of several products characteristic of free radical oxidation by $RO_2\bullet$ and $HO\bullet$, including cumene hydroperoxide, acetophenone, cumyl alcohol, and isopropylphenols. These findings suggest that photolysis of the natural organics in water produces the free radical oxidants.

The processes observed with cumene are summarized in the following scheme:

$$\text{natural organic} \xrightarrow{h\nu} HO\bullet + RO_2\bullet \tag{4.80}$$

$$RO_2\bullet + CuH \longrightarrow RO_2H + Cu\bullet \tag{4.81}$$

$$Cu\bullet + O_2 \longrightarrow CuO_2\bullet \tag{4.82}$$

$$CuO_2\bullet \xrightarrow{\text{several steps}} CuO_2H + CuOH + PhCOMe \tag{4.83}$$

$$HO\bullet + CuH \longrightarrow HO\overset{\bullet}{Ph}CHMe_2 \tag{4.84}$$

$$HO\overset{\bullet}{Ph}CHMe_2 + O_2 \longrightarrow HOPhCHMe_2 + HO_2\bullet \tag{4.85}$$

Separate experiments in pure, sterile water with several free radical initiators in the dark, showed that cumene reacts with $RO_2\bullet$ to give only side chain oxidation products (hydroperoxide, alcohol, and ketone) while $HO\bullet$ reacts mostly by addition to the ring to give phenols. Thus the ratio of side-chain products (SP) to ring products (R) is a measure of the relative abundance of $RO_2\bullet$ and $HO\bullet$ oxidants. The ratio of products from side-chain and ring oxidation can vary widely from one water source to another as well as within one source at different times.

Concentrations of radical oxidants in these natural waters can be calculated from the rates of production of ring and side-chain products and a knowledge of the rate constants for reaction of cumene with $RO_2\bullet$ and $HO\bullet$.

$$d[\mathrm{CuH}]/dt = (k_{\mathrm{HO}}[\mathrm{HO}] + k_{\mathrm{RO_2}}[\mathrm{RO_2}\bullet])[\mathrm{CuH}] = k[\mathrm{CuH}] \qquad (4.86)$$

$$[\mathrm{RP}] = k_{\mathrm{HO}}[\mathrm{HO}][\mathrm{CuH}]_o(1 - e^{-kt})k^{-1} \qquad (4.87)$$

$$[\mathrm{SCP}] = k_{\mathrm{RO_2}}[\mathrm{RO_2}\bullet][\mathrm{CuH}]_o(1 - e^{-kt})k^{-1} \qquad (4.88)$$

Table 4.5 summarizes results of calculations using equations (4.87) and (4.88). These values for $[\mathrm{RO_2}\bullet]$ are corroborated by studies of the rate of oxidation of pyridine to its N-oxide in natural water. The N-oxide is formed from reaction with $\mathrm{RO_2}\bullet$ but not with $\mathrm{HO}\bullet$, although the latter oxidant does oxidize the carbon ring to give hydroxypyridines. Values of $[\mathrm{RO_2}\bullet]$ and $[\mathrm{HO}\bullet]$ tabulated in Table 4.5 are for near surface conditions in water; in eutrophic waters at depths of several meters or more, light penetration will be small and the average concentration of radicals will be reduced accordingly.

TABLE 4.5. CONCENTRATIONS OF OXIDANTS IN NATURAL WATERS

Water	$[\mathrm{RO_2}\bullet]^{a,b} \times 10^{9}$ M	$[\mathrm{HO}\bullet]^{b,c} \times 10^{17}$ M
Aucilla River	2.8	1.8
Boronda Lake	9.5	0.15
Coyote Creek	9.1	1.6

[a] $[\mathrm{RO_2}\bullet] = k[\mathrm{S}]/[\mathrm{CuH}]_o k_{\mathrm{RO_2}}(1 - e^{-kt})$.

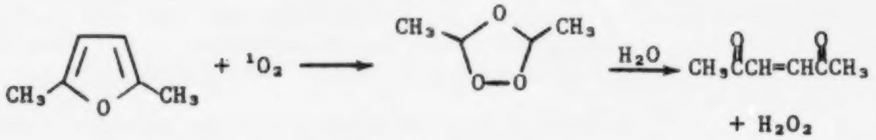
[b] Near surface values (see text).

[c] $[\mathrm{HO}\bullet] = k[\mathrm{R}]/[\mathrm{CuO}]_o k_{\mathrm{HO}}(1 - e^{-kt})$.

This investigation by Mill et al. (1977) is the only quantitative study of radical oxidations in waters at low concentrations. The results leave open the question of whether some oxidation is due to triplet diradicals as well as $\mathrm{RO_2}\bullet$ and the possibility that some $\mathrm{HO}\bullet$ radicals are generated by photolysis of the cumene hydroperoxide product.

Singlet Oxygen

Zepp and coworkers (1977) have investigated the formation of singlet oxygen in a variety of natural waters using the selective and reactive probe dimethylfuran (DMFN), which gives cis-diacetylethylene via 1,4-addition of $^1O_2$ (Foote et al., 1967).



(4.89)

Although this same product might conceivably form by a free radical oxidation, the specific accelerating effect of D_2O and inhibiting effect of diazobicyclooctane (DABCO) on the rate strongly point to participation by $^1O_2$ in the rate-controlling step. Quantum yields for product formation varied by a factor of 5 (from 0.02 to 0.1) for a factor of 23 in optical absorbance in the water samples used. A kinetic analysis of these reactions was made by following the loss of DMFN with time and using the usual relation

$$d(\mathrm{DMFN})/dt = k_{OX}[^1O_2][\mathrm{DMFN}] \tag{4.90}$$

to evaluate $k_{OX}[^1O_2]$, which in turn, can be related to the half-life of the reaction by

$$[^1O_2] = \frac{\ln 2}{t_{1/2}k_{OX}} \tag{4.91}$$

k_{OX} for DMFN is 4×10^8 M^{-1} s^{-1} (Merkel and Kearns, 1972). Values of $[^1O_2]$ varied from $(< 0.1\text{-}22) \times 10^{-13}$ M for an average value of 1×10^{-12} M.

As the authors point out and is shown also in Table 4.4, this concentration of singlet oxygen can be important for oxidation of a variety of organic chemicals, including amino acids, mercaptans, sulfides, and polycyclic aromatics. Half-lives for most of these chemicals are in the range of 1 to 10 hours in reactions with this concentration of $^1O_2$.

4.7.5 Design of Laboratory Test Methods

$RO_2\cdot$ Oxidation Test

Section 4.7.3 shows how it is possible to evaluate k_{RO_2} for reaction of $RO_2\cdot$ and CH bonds if a free radical initiator is used to provide a known rate of production of $RO_2\cdot$ (R_i) and t-BuO_2H is added to convert all $RO_2\cdot$ and $RO\cdot$ to t-$BuO_2\cdot$. k_{RO_2} can be evaluated by the loss of chemical directly or relative to that of a standard chemical having a known k_{RO_2}. A suitable free radical source for use in either system is azobis(2-carbomethoxy-propane), MAB, a well-characterized azo initiator (Mortimer et al., 1964) slightly soluble in water (1×10^{-3} M) as well as in organic solvents. Water alone with 1 M t-BuO_2H is the first choice as solvent, but because many chemicals have low solubility or volatilize rapidly from water and because solvent effects in radical oxidations are small, addition of acetonitrile up to 10% by volume is acceptable and possibly preferable wherever solubility or volatilization is a problem.

Equation (4.23) describes a relative rate measurement in which the measured variables are alcohols [SOH] and [ROH] derived from standard and unknown chemicals, SH and RH. Assuming that conventional analyses (gc or lc) will allow reliable estimates of products at 5×10^{-6} M, and that 10% conversions of starting chemicals do not invalidate use of equation (4.23) then the initial concentrations of SH and RH can be $\sim 5 \times 10^{-5}$ M or higher.

Standard chemicals for relative measurements must meet specific chemical and physical requirements: oxidation must occur readily only at one type of CH bond; the compound must be soluble at pH 7 to the extent of $\sim 10^{-4}$ M, must be relatively nonvolatile, and must give an alcohol product that can be analyzed easily. No ideal standard has been tested but some possibilities include 4-isopropylpyridine, benzylpyridine and acetylpyridine. Rate constants (k_{OX}) for these chemicals have not been measured but they probably lie in the range of 0.5 to 10 M^{-1} s^{-1}.

Another experimental approach to measuring k_{RO_2} involves application of equation (4.34) where direct loss of the chemical is measured in an aqueous solution containing a known concentration of MAB and sufficient t-BuO₂H to scavenge all $RO_2\bullet$ and $RO\bullet$ radicals. If the MAB concentration is chosen as 1×10^{-4} M, the initial steady state concentration of t-$BuO_2\bullet$ will be

$$[RO_2\bullet] = \left(\frac{R_i}{2k_t}\right)^{\frac{1}{2}} = \left(\frac{7.6 \times 10^{-11}}{3.3 \times 10^{3}}\right)^{\frac{1}{2}} = 1.5 \times 10^{-7} \text{ M} \qquad (4.92)$$

Therefore the initial rate of oxidation of 5×10^{-5} M chemical having k_{RO_2} of 100 M^{-1} s^{-1} is

$$d[C]/dt = k_{RO_2}[C][t\text{-}BuO_2\bullet] \qquad (4.93)$$

$$= 100 \times (5 \times 10^{-5}) \times (1.5 \times 10^{-7})$$

$$= 7.5 \times 10^{-10} \text{ M s}^{-1}$$

During each initial hour the loss would be 2.7×10^{-6} M; in ten hours the loss would be close to 2.7×10^{-5} M or 5%. In the environment, where $[RO_2\bullet] \sim 10^{-9}$ M, this same chemical would have a half-life of 80 days at 50°C but about 300 days at 25°C. Therefore, a chemical reacting at only this rate may be regarded as essentially unreactive in oxidation.

We can readily calculate that, if a chemical oxidizes only at CH bonds with a half-life in the environment of less than 3 months (80 days), k_{OX} at 50° is > 300 M^{-1} s^{-1}. This chemical will, in turn, oxidize in the MAB/t-BuO₂H solution at 2.5 times the rate of the example cited above and will half oxidize in 4.5 hours; 25% loss will occur in about 2.1 hours.

Oxidation rate constants for chemicals that react with $RO_2\bullet$ at OH, NH, or SH bonds must be evaluated differently from those that oxidize at CH bonds because of their rapid reactions ($k_{OX} > 10^{3}$ M^{-1} s^{-1}). Added t-BuO₂H is not used. At this time the simple test procedure can give only a lower limit to

k_{OX} based on a loss rate for the chemical equal to half the production rate of $RO_2\bullet$, if $k_p > 10^4$ M^{-1} s^{-1}.

For example, if a phenol is present initially at 5 x 10^{-5} M, 25% will be oxidized in 27 hr at 50° with 1 x 10^{-4} M MAB if $k_{OX} > 10^4$ M^{-1} s^{-1}. This calculation assumes that one phenol is oxidized for every two $RO_2\bullet$ produced (zero order rate law) and

$$[RO_2\bullet]_t = 0.4[MAB]_o(1 - e^{-4x10^{-6}t}) \qquad (4.94)$$

where $[RO_2\bullet]_t$ is the total concentration of $RO_2\bullet$ produced in t hours.

$^1O_2$ Oxidation Test

Rate constants for reaction of $^1O_2$ are readily measured by using a reference chemical together with the test chemical and a sensitizer such as rose bengal (RB), which efficiently generates $^1O_2$. Rose bengal is soluble in water and in some cosolvents and absorbs light at 555 nm (rose red), well beyond the absorption spectra of most chemicals apart from other dyes. A solution at 10^{-5} M RB absorbs over 90% of the light at 555 nm.

The very low concentrations of chemicals used in this test often are necessitated by solubility limits, but also are preferred because of closer relevance to environmental conditions and because low concentrations minimize secondary reactions of products and starting chemicals. Pure water is preferred as solvent but at least for rate studies there appears to be little harm in using up to 10% acetonitrile. Using the reference chemical and test chemical in the same solution eliminates variables associated with the lamp and dye but they may be used separately in a merry-go-round apparatus.

No special light source is needed for irradiation, but if the chemical is sensitive to near uv and visible light (photolysis protocol), a cut-off filter removing all light below 450 nm is necessary. Ordinary incandescent lamps or sunlamps are quite satisfactory for this test as is a merry-go-round photolysis unit.

Light intensities and therefore reaction times will vary with the source, its filter system, and the distance from the reaction system. A standard merry-go-round, which uses a 400-watt mercury lamp (filtered to pass only light around 546 nm), delivers about 4 x 10^{-8} einsteins s^{-1} per 2 ml of reaction solution or about 2 x 10^{-5} einsteins ℓ^{-1} s^{-1}. If enough rose bengal is used to absorb 90% of the light (about 10^{-5} M) at 555 nm (λ_{max}) and the quantum yield for $^1O_2$ formation is 0.8, we can readily calculate that the rate of $^1O_2$ formation is 1.4 x 10^{-5} M s^{-1}. Since the rate of loss of $^1O_2$ in dilute aqueous solution of chemicals is governed only by the first-order process where k_d = 1 x 10^6 s^{-1}, the steady-state concentration of $^1O_2$ is 1.4 x 10^{-11} M.

A chemical with moderate reactivity toward $^1O_2$ such as 2-methyl-2-pentene (k_{OX} = 1 x 10^6 M^{-1} s^{-1}) will oxidize with a rate constant of 1.4 x 10^{-5} s^{-1} and will be one-quarter oxidized in about 5 hours. By contrast an eneamine with a rate constant 10 times larger will be 95% oxidized in the same time period. A variety of chemicals may be useful as reference chemicals for relative reactivity measurements toward $^1O_2$. Among the criteria for selecting suitable reference chemicals are reactivity, solubility in water, lack of direct photochemical reaction, and preferably nonperoxidic products, i.e., no reaction by the ene mechanism or rapid reaction of ene products with water. Some chemicals that may meet these criteria are allylthiourea, dihydropyran, aliphatic eneamines and vinyl ethers and some furans. Rate constants for reactions of these chemicals or classes are shown in Table 4.4.

The principal problem in selecting a standard or reference chemical is choosing one that is not greatly different in reactivity from the test chemical in order to evaluate with some accuracy the relation.

$$\ln(C_o/C)/\ln(S_o/S) = k_C/k_S \qquad (4.95)$$

where C and S refer to the test and standard chemicals, respectively. If the two chemicals differ in their reactivity by a factor of 10, loss of half of the more reactive chemical will be accompanied by loss of only 6% of the less reactive chemical, an unsuitably small change. Since chemicals having similar structural units will often have similar reactivities, selection of a reference chemical as close as possible in structure to the test chemical will help minimize differences in reactivity and minimize the number of analyses.

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CHAPTER 5. ATMOSPHERIC CHEMISTRY

by

D. G. Hendry

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5. ATMOSPHERIC CHEMISTRY

5.1 INTRODUCTION

Chemical processes compete with physical processes in determining the fate of chemicals entering the atmosphere. The more reactive compounds (lifetimes of ∿ 1 day) will react rapidly within the boundary layer of the atmosphere immediately adjacent to the earth's surface where the emissions generally occur. Less reactive compounds will be distributed by diffusion and turbulent mixing into the remainder of the troposphere and in some cases will be reasonably well mixed in the entire troposphere before appreciably reacting. Finally, those compounds that are stable to the oxidative and photic environment of the troposphere, and are not removed by physical process such as rainout, will gradually diffuse into the stratosphere where additional loss mechanisms exist--the most important of which is photolysis in the 150-300 nm region of the solar spectrum. To understand the effects of industrial chemicals on the environment, it is important to anticipate what processes are critical for each chemical and in what regions of the atmosphere they will occur.

The important chemical processes in the atmosphere are all the result of the absorption of sunlight in the atmosphere. In some cases the chemical compounds can absorb sunlight directly and thereby undergo reaction. Other compounds only react with reactive species, such as ozone and hydroxyl radicals formed as the consequence of absorption of solar energy by other species and the subsequent complex chemistry that follows. The three basic atmospheric reactions that account for reaction of organic compounds are

(1) Direct photolysis
(2) Reaction with hydroxyl (OH) radical
(3) Reaction with ozone (O_3).

These processes, as well as methods to determine their importance for specific compounds, will be discussed in detail in this chapter. However, they compete with a number of physical processes, including:

(1) Dilution
(2) Dry deposition
(3) Sorption to particulate
(4) Rainout and washout
(5) Diffusion to stratosphere.

Dilution generally accounts for a very rapid reduction of concentration of emissions, but it does not result in any loss of mass from the atmosphere. Dilution affects all compounds equally, whereas the other physical processes are compound-specific. Dry deposition is important for compounds that have an affinity for reaction or sorption on surfaces such as soils, water bodies, plants and man-made structures. Once a compound is sorbed to a particulate, its fate is determined by factors that affect the particulate, including rainout, washout, conglomeration, and fallout; desorption is also a possibility because dilution reduces the concentration of free compound around the particulate. Rainout and washout affects compounds with high water solubility, depositing them in water bodies and on land. In either case, the pollutant may be revolatilized depending on the atmospheric conditions and the affinity of the compound for solution in water or sorption to soil.

Atmospheric sources and fates of both natural and man-made chemicals are summarized in Figure 5.1. Heterogeneous chemistry associated with the chemicals sorbed to the particulate phase is not included. We currently have no data on how important such processes can be but we expect them to be limited to a small group of compounds of low volatility that strongly sorb to the particulate phase.

This protocol is concerned solely with the chemistry of compounds in the vapor phase. The reactions considered include direct photochemical reaction and reactions with OH radical and with ozone. The protocol does not consider physical processes, but these processes are expected to be important for only a small number of compounds.

5.2 OBJECTIVE

The main objective of this chapter is to develop two-tier test procedures to determine the rate constants of atmospheric chemical processes that control the lifetime of chemical compounds in the atmosphere, including direct photolysis and reactions with ozone and hydroxy radical.

5.3 SUMMARY

A two-tier series of tests has been outlined to evaluate the lifetime of compounds in the atmosphere as determined by photolysis and reactions with hydroxyl radical (OH) and ozone (O_3).

The first tier of tests screens these three pathways and estimates the approximate importance of each. An upper limit for the rate of photolysis is obtained by assuming that reaction occurs with a quantum efficiency of unity and by equating the rate of reaction with the rate of absorption of light. The latter rate is determined by combining ultraviolet-visible absorption spectral data with the solar spectral intensities. A hand method of integrating absorption and solar intensity data for various times of the year is provided.

Estimates of the rate constants for reaction with hydroxy radical and ozone are based on analogy to other structures. From these rate constants and estimates of the environmental concentrations of OH and ozone, estimates of the lifetime are made.

Once the relative importance of the three basic processes is determined, the rate constants for those processes that clearly dominate are measured in detailed tests. These detailed tests constitute the second tier of tests.

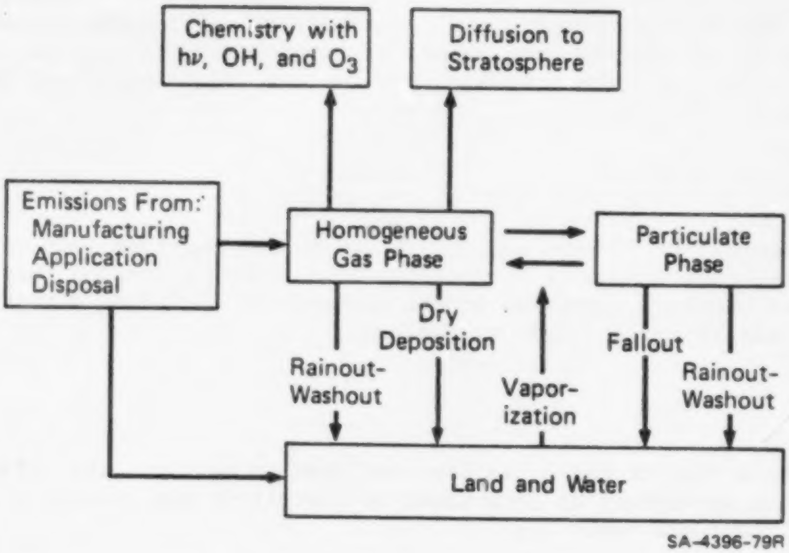

Chemistry with
hν, OH, and O3
Diffusion to
Stratosphere
Emissions From:
Manufacturing
Application
Disposal
Homogeneous
Gas Phase
Particulate
Phase
Dry
Deposition
Rainout-
Washout
Vapor-
ization
Fallout
Rainout-
Washout
Land and Water
SA-4396-79R

FIGURE 5.1 FATE OF GASEOUS EMISSIONS

The rate constant for reaction with OH is determined by measuring the rate of loss of the chemical relative to the loss of a standard compound with known OH rate constants in the presence of OH generated from nitrous acid photolysis. If the reaction with ozone appears to be important, the rate constant will be determined by following the disappearance of ozone in the presence of the compound.

For the photochemical reaction, the quantum yield at one wavelength is measured, generally in the solar spectrum, and is combined with the rate of absorption of light determined in the first tier to obtain the rate of photolysis.

5.4 CONCLUSIONS AND RECOMMENDATIONS

The rates of reaction of most chemicals in the atmosphere can be readily determined using relatively simple laboratory measurements. The important chemical processes in the atmosphere that can be evaluated using techniques outlined in this report are photolysis by direct absorption of solar radiation, and oxidation by reactions with both hydroxyl radical and ozone.

Further research is needed to determine the effect of particulate absorption on environmental lifetimes. If this process deactivates compounds toward further chemical reactions, then environmental lifetimes can be increased, but if additional reaction pathways exist for absorbed materials, then the environmental lifetimes will be decreased.

5.5 SCREENING TESTS

The purpose of the screening tests is to set upper limits or approximate values for the half-lives for photochemical reaction and reaction with ozone and OH.

5.5.1 Photochemical Reaction: Absorption Spectrum

This screening test involves measuring the vapor phase uv spectrum in air over the solar spectrum. A maximum rate of photolysis is calculated by assuming a quantum yield of unity over all wavelengths where absorption occurs in the solar spectrum.

The following are required for this procedure:

(1) A uv spectrophotometer capable of scanning the region 290 to 800 nm.
(2) A uv gas cell, with quartz windows and suitable gas handling system for measuring the pressure of vapor in cells.

Figure 5.2 shows a suitable gas handling system for charging the uv cell. Mercury should not be used in the apparatus in either the pumping or pressure measuring systems. Stopcocks should be high vacuum O-ring stopcocks; if ground glass stopcocks are used, a lubricant should be used that does not absorb the compound being studied.

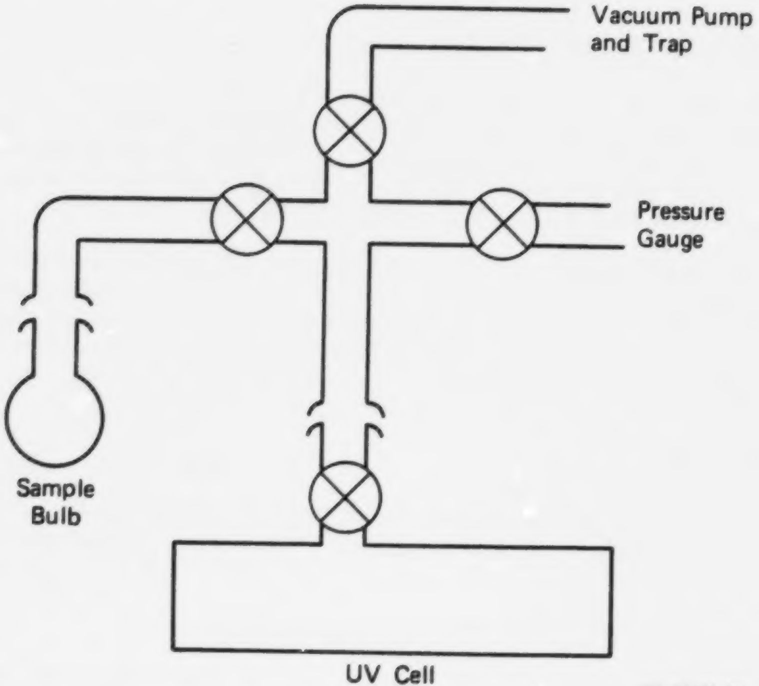

Vacuum Pump and Trap
Pressure Gauge
Sample Bulb
UV Cell
SA-4396-80

FIGURE 5.2 GAS HANDLING SYSTEM FOR CHARGING UV CELL

The following procedure is recommended for use with the apparatus shown in Figure 5.2. The uv cell is attached to the apparatus by the vacuum-tight joint (10 mm o-ring) and evacuated to less than 10^{-5} torr, if possible, but to at least one-hundredth of the pressure of the compound to be introduced into the cell. Several milliliters of liquid compound are then placed in the sample reservoir and degassed by repeated freezing, pumping, and thawing for three cycles. Then the compound is allowed to warm to room temperature and a sample is allowed to expand into the uv cell and manometer. The pressure is read and the stopcocks to the cell and reservoir are closed. The vapor in the connecting tube is pumped out. Then air, dried over molecular sieves, is allowed to fill the connecting tubing first and then allowed to slowly enter the uv cell until atmospheric pressure is obtained. Then the stopcock on the cell is closed and the cell is warmed to 75°C for one hour to enhance mixing. Then the uv cell is allowed to cool, disconnected from the apparatus, and placed in the uv spectrophotometer. The uv-visible spectrum is then measured relative to a matched cell filled with air according to manufacturers' directions using minimum slit openings. This procedure is to be repeated at two other pressures of compound. The pressures should differ by at least a factor of two and preferably five to ten, providing the absorption is sufficiently strong at the lower pressure to provide an absorbance one-tenth of the more sensitive scale. However, this limit depends on instrument stability, which is partly a function of the slit opening.

The data are then tabulated, and the cross sections or absorption coefficients can be determined from Beer-Lambert Law (equation 5.1) in the form

$$\sigma = (\ell C)^{-1} \ln \frac{I_o}{I} \qquad (5.1)$$

where σ is the cross section in cm^2 $molec^{-1}$, ℓ is the pathlength in cm, C is the concentration in molec cm^{-3}, and I_o and I are the intensities of incident and final light in photons cm^2. From the consistency of the data at three pressures plus estimates of possible deviations, it will be possible to determine if there is deviation from Beer-Lambert Law. In cases where there is a consistent variation between the cross sections, determined at different pressures, the low pressure values are preferred, providing that the precision of the measurements is ± 25%.

The cross sections are combined at each wavelength range with the solar intensities from Tables 5.1, 5.2, and 5.3 to obtain the average seasonal photolysis rate constants at 10°, 30°, and 50°N latitude. This is done using the procedure in Section 5.7.2, assuming unit quantum efficiency. Because of the latter assumption, the calculated rate constant is an upper limit ($\bar{k}_p$)

$$\bar{k}_p = \Sigma \sigma_\lambda J_\lambda' \qquad (5.2)$$

The half-life, which will be a lower limit, is

$$\bar{t}^p_{\frac{1}{2}}(\text{days}) = \ln 2/\bar{k}_p \qquad (5.2a)$$

TABLE 5.1. J_λ' VALUES AT 10° N LATITUDE[a]

Wavelength Range, nm	Solstice		Equinox	Season Average	
	Summer	Winter		Spring/Summer	Fall/Winter
285-295	0	0	0	0	0
295-305	6.39 17	3.31 17	6.38 17	6.63 17	4.6 17
305-315	9.701 18	6.679 18	9.522 18	9.815 18	7.91 18
315-325	2.451 19	1.852 19	2.386 19	2.457 19	2.685 19
325-335	4.474 19	3.518 19	4.341 19	4.468 19	3.877 19
335-345	4.945 19	3.957 19	4.789 19	4.828 19	4.321 19
345-355	5.666 19	4.605 19	5.479 19	5.638 19	4.735 19
355-365	5.85 19	4.758 19	5.656 19	5.820 19	4.925 19
365-375	7.301 19	5.976 19	7.655 19	7.226 19	6.357 19
375-385	7.157 19	5.891 19	6.913 19	7.125 19	6.343 19
385-395	7.329 19	6.065 19	7.075 19	7.278 19	6.663 19
395-405	1.004 20	8.341 19	9.687 19	9.966 19	8.927 19
405-415	1.275 20	1.063 20	1.23 20	1.265 20	1.135 20
415-425	1.331 20	1.114 20	1.283 20	1.320 20	1.187 20
425-435	1.349 20	1.133 20	1.30 20	1.338 20	1.205 20
435-445	1.491 20	1.256 20	1.436 20	1.478 20	1.339 20
445-455	1.718 20	1.449 20	1.655 20	1.702 20	1.538 20
455-465	1.857 20	1.568 20	1.789 20	1.840 20	1.664 20
465-475	1.914 20	1.619 20	1.843 20	1.896 20	1.716 20
475-485	1.941 20	1.645 20	1.869 20	1.922 20	1.742 20
485-495	1.945 20	1.652 20	1.873 20	1.926 20	1.747 20
495-515	3.970 20	3.370 20	3.823 20	3.932 20	3.565 20
515-535	4.013 20	3.41 20	3.863 20	3.974 20	3.605 20
535-555	3.995 20	3.398 20	3.846 20	3.956 20	3.591 20
555-575	4.053 20	3.446 20	3.902 20	4.014 20	3.692 20
575-595	4.197 20	3.573 20	4.040 20	3.659 20	3.774 20
595-635	8.529 20	7.235 20	8.211 20	8.446 20	7.652 20
635-675	8.976 20	7.658 20	8.637 20	8.884 20	8.077 20
675-715	9.077 20	7.778 20	8.732 20	8.961 20	8.186 20
715-755	8.744 20	7.514 20	8.410 20	8.650 20	7.897 20
755-795	8.460 20	7.287 20	8.135 20	8.367 20	7.648 20

[a] Second number in column is the power of ten by which the first number is multiplied.

[b] Units are in photons cm^{-2} day^{-1} as discussed in text.

TABLE 5.2. J_λ' VALUES AT 30°N LATITUDE[a,b]

Wavelength Range, nm	Solstice				Equinox		Season Average			
	Summer		Winter				Spring/Summer		Fall/Winter	
285-295	1.0	16	0		0		1.18	15	0	
295-305	7.40	17	6.80	16	3.98	17	6.24	17	1.78	17
305-315	1.09	19	2.83	18	7.49	18	9.77	18	4.60	18
315-325	2.74	19	1.00	19	2.03	19	2.50	19	1.41	19
325-335	4.98	19	2.11	19	3.82	19	4.58	19	2.79	19
335-345	5.49	19	2.48	19	4.28	19	5.07	19	3.20	19
345-355	6.28	19	3.11	19	4.96	19	5.82	19	3.68	19
355-365	6.49	19	3.10	19	5.13	19	6.01	19	3.92	19
365-375	8.09	19	3.95	19	6.43	19	7.51	19	4.96	19
375-385	7.93	19	3.95	19	6.33	19	7.36	19	4.92	19
385-395	8.12	19	4.12	19	6.51	19	7.55	19	5.09	19
395-405	1.11	20	5.72	19	8.94	19	1.03	20	7.04	19
405-415	1.41	20	7.36	19	1.14	20	1.31	20	8.64	19
415-425	1.47	20	7.80	19	1.19	20	1.37	20	9.37	19
425-435	1.49	20	7.99	19	1.21	20	1.39	20	9.67	19
435-445	1.65	20	8.93	19	1.34	20	1.54	20	1.08	20
445-455	1.90	20	1.04	20	1.55	20	1.77	20	1.25	20
455-465	2.05	20	1.13	20	1.67	20	1.92	20	1.35	20
465-475	2.12	20	1.17	20	1.73	20	1.98	20	1.40	20
475-485	2.15	20	1.19	20	1.75	20	2.01	20	1.42	20
485-495	2.15	20	1.20	20	1.76	20	2.01	20	1.43	20
495-515	4.39	20	2.45	20	3.59	20	4.10	20	2.92	20
515-535	4.44	20	2.49	20	3.63	20	4.15	20	2.96	20
535-555	4.42	20	2.49	20	3.62	20	4.13	20	2.95	20
555-575	4.48	20	2.52	20	3.67	20	4.19	20	2.99	20
575-595	4.64	20	2.62	20	3.80	20	4.34	20	3.11	20
595-635	9.44	20	5.39	20	7.70	20	8.81	20	6.34	20
635-675	9.92	20	5.72	20	8.15	20	9.28	20	6.72	20
675-715	1.00	21	5.85	20	8.27	20	9.39	20	6.84	20
715-755	9.67	20	5.70	20	7.98	20	9.05	20	6.64	20
755-795	9.35	20	5.57	20	7.74	20	8.76	20	6.46	20

[a] Second number in column is the power of ten by which the first number is multiplied.

[b] Units are in photons cm^{-2} day^{-1} as discussed in text.

TABLE 5.3. J_{λ}' VALUES AT 50°N LATITUDE[a,b]

Wavelength Range, nm	Solstice		Equinox	Season Average	
	Summer	Winter		Spring/Summer	Fall/Winter
285-295	0	0	0	0	0
295-305	5.7 17	6.0 14	1.12 17	3.763 17	2.55 16
305-315	1.005 19	2.981 17	3.945 18	7.724 18	1.398 18
315-325	2.680 19	1.857 18	1.317 19	2.173 19	5.699 18
325-335	5.0 19	5.429 18	2.714 19	4.162 19	1.314 19
335-345	5.577 19	7.118 18	3.163 19	4.700 19	1.597 19
345-355	6.446 19	8.513 18	3.86 19	5.495 19	1.984 19
355-365	6.659 19	9.536 18	3.923 19	5.670 19	2.057 19
365-375	8.341 19	1.248 19	4.985 19	7.130 19	2.648 19
375-385	8.204 19	1.279 19	4.967 19	7.038 19	2.646 19
385-395	8.427 19	1.070 19	5.165 19	7.255 19	2.816 19
395-405	1.157 20	1.951 19	7.161 19	9.987 19	3.949 19
405-415	1.472 20	2.569 19	9.194 19	1.274 20	5.132 19
415-425	1.540 20	2.792 19	9.715 19	1.337 20	5.478 19
425-435	1.564 20	2.915 19	9.938 19	1.361 20	5.652 19
435-445	1.732 20	3.326 19	1.109 20	1.510 20	6.366 19
445-455	1.996 20	3.91 19	1.283 20	1.743 20	7.413 19
455-465	2.159 20	4.30 19	1.392 20	1.886 20	8.087 19
465-475	2.227 20	4.533 19	1.443 20	1.948 20	8.444 19
475-485	2.261 20	4.685 19	1.471 20	1.981 20	8.659 19
485-495	2.268 20	4.769 19	1.483 20	1.983 20	8.758 19
495-515	4.629 20	9.789 19	3.026 20	4.060 20	1.791 20
515-535	4.682 20	1.001 20	3.069 20	4.109 20	1.823 20
535-555	4.664 20	1.002 20	3.062 20	4.095 20	1.822 20
555-575	4.732 20	1.014 20	3.104 20	4.153 20	1.845 20
575-595	4.903 20	1.063 20	3.228 20	4.308 20	1.926 20
595-635	9.935 20	2.227 20	6.631 20	8.749 20	3.983 20
635-675	1.048 21	2.463 20	7.015 20	9.253 20	3.428 20
675-715	1.061 21	2.610 20	7.165 20	9.40 20	4.431 20
715-755	1.023 21	2.644 20	6.977 20	9.089 20	4.370 20
755-795	9.902 20	2.648 20	6.809 20	8.821 20	4.311 20

[a] Second number in column is the power of ten by which the first number is multiplied.

[b] Units are in photons cm^{-2} day^{-1} as discussed in text.

5.5.2 Screening Test for Reaction of OH

For the purposes of screening the importance of reaction with OH, the method of rate constant estimation outlined in Section 5.7.3 is applied. The rate constant is expressed by the equation

$$k_{OH} = \sum_{i=1}^{i} n_i \alpha_{Hi} \beta_{Hi} k_{Hi} + \sum_{j=1}^{j} n_j \alpha_{Ej} k_{Ej} + \sum_{\ell=1}^{\ell} n_e \alpha_{A\ell} k_{A\ell} \qquad (5.3)$$

The first summation accounts for reaction of all reactive hydrogen atoms within the molecule. The term k_{Hi} is the reactivity of the hydrogen atoms from Table 5.4, taking into account the position and degree of substitution on the adjacent atom by alkyl, vinyl, phenyl, C(O)-, O-, S-, and N- groups. The terms α_{Hi} and β_{Hi} account for the effect of groups in the α-position and β-position on the carbon-hydrogen bond and are also defined in Table 5.4. These terms are applied for each α and β substituent; thus,

$$\alpha_{H_i} = \Pi\alpha'_{Hi} \cdot \alpha''_{Hi} \cdots \text{ and } \beta_{H_i} = \Pi\beta'_{Hi} \cdot \beta''_{H_i} \cdots$$

The term n_i accounts for the repetition of the i^{th} carbon-hydrogen bond.

The second summation accounts for the reactivity of all carbon-carbon double bonds in the molecule. The term k_E is the intrinsic reactivity of each double bond, taking into account the degree of substitution, whereas α_E accounts for the effect of any halogen substituted directly to the double bond. These terms are defined in Table 5.5. n_j accounts for the repetition of each unique double bond.

The third summation accounts for addition of OH to aromatic rings in the molecule. k_A is the intrinsic reactivity of the ring, taking into account the degree of alkyl substitution. α_A accounts for halogen substituents in the ring. Both k_A and α_A are defined in Table 5.6.

The sum of the three terms determines k_{OH} (in cm^3 $molec^{-1}$) for the compound. Examples of this calculation are given in Figure 5.3.

The half-life for reaction with OH is

$$t_{1/2}^{OH} = \ln 2/k_{OH}[OH] \qquad (5.4)$$

Assuming an average ground level concentration over the year of OH = 10^6 $molec/cm^3$ (1.7×10^{-8} ppm) based on the discussion in Section 5.7.4, the half-life is

$$t_{1/2}^{OH}(\text{seconds}) = 6.93 \times 10^{-7}/k_{OH} \qquad (5.4a)$$

TABLE 5.4. ABSTRACTION RATE CONSTANTS (k_H) FOR REACTION OF OH WITH GENERALIZED GROUPS AND VALUES OF INDUCTION FACTORS (α_H AND β_H)

Group[a]	10^{12} k_H[b] (per hydrogen)		α_H	β_H
C_SCX_2-H	0.065 ± 0.013	H	1.0	1.0
$(C_S)_2CX$-H	0.55 ± 0.07	Cl, Br	2.4 ± 0.6	0.4 ± 0.1
$(C_S)_3C$-H	2.9 ± 0.58	F	1.0	0.3 ± 0.1
C_D-H	0.01 ± 0.002	OH	2.0 ± 0.05	1.0
C_DCX_2-H	0.3 ± 0.1	O-alkyl	6.0 ± 2.0	1.0
$(C_S)(C_D)CX$-H	2.5 ± 1.0	$O\overset{O}{\overset{\|}{C}}-$	1.0	1.0
$(C_S)_2(C_D)C$-H	4.0 ± 1.5	C-	1.3 ± 0.2	1.0
		N<	100 ± 50	1.0
		S-	200 ± 100	1.0
$-\overset{O}{\overset{\|}{C}}-H$	17 ± 4			
S-H	2.6 ± 1.3	all cases	1.0	1.0
C_DO-H	1.7 ± 0.8			

[a] C_S = Saturated carbon, -O, -C=O, or -S; C_D = unsaturated carbon as in vinyl or phenyl groups; X = H, F, Cl, or Br.

[b] Rate constant expressed as cm^3 $molec^{-1}$ s^{-1}.

TABLE 5.5. ADDITION RATE CONSTANTS (k_E) FOR REACTION OF OH WITH CARBON-CARBON BOND, AND VALUES OF INDUCTION FACTORS (α_E)

Substituent	$10^{12}k^a$ (per double bond)	Substituent α_E
none (ethene)	7.9	
1-alkyl	27 ± 5	
1,1-dialkyl	50 ± 10	F = 0.5 ± 0.3
1,2-dialkyl		Cl,Br = 0.7 ± 0.3
cis	60 ± 12	
trans	70 ± 14	
trialkyl	80 ± 16	
tetraalkyl	150 ± 30	
vinyl or phenyl	80 ± 20	
OMe	33	

[a] Rate constant expressed as cm^3 $molec^{-1}$ s^{-1}.

TABLE 5.6. ADDITION RATE CONSTANTS (k_A) FOR REACTION OF OH WITH AROMATIC RINGS, AND VALUES OF INDUCTION FACTORS (α_A)

Substituent	$10^{12}k^a$	Substituent	α_A
H	1.4	H	1.0
alkyl	5.0 ± 2	Cl,F,Br	< 1.0
dialkyl	12 ± 4		
1,2,3-trialkyl	10 ± 5		
1,2,4-trialkyl	25 ± 5		
1,3,5-trialkyl	49 ± 5		
methoxy	17 ± 5		
OH plus alkyl	34 ± 10		
$-\overset{O}{\overset{\|}{C}}H$	< 1.0		

[a] Rate constant expressed as cm^3 $molec^{-1}$ s^{-1}.

1,2-Dichloroethane: $ClCH_2CH_2Cl$

$H_2CClCCl$: $4(0.065 \pm .013)(2.4 \pm 0.6)(0.4 \pm 0.1) = 0.25(0.11-0.47)$

Measured value (Table 5.14) = 0.22

1,1-Dichloroethane: Cl_2CHCH_3

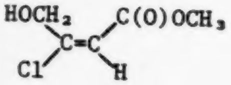
$HCCl_2C$: $(0.065 \pm .013)(2.4 \pm 0.6)^2 = 0.37(0.17 - 0.70)$

H_3CCCl_2: $3(0.065 \pm .013)(0.4 \pm 0.1)^2 = 0.03(0.015 - 0.06)$

$\Sigma = 0.40(0.17 - 0.72)$

Measured value (Table 5.14) = 0.26

3-Chloro-4-hydroxy-cis-butenoic methyl ester:



cis-C=C: $(60 \pm 12)(0.7 \pm .3) = 42\ (15 - 72)$

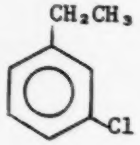
$-CH_2-$: $2(2.5 \pm 1)(2.0 \pm 0.5) = 10\ (4.4 - 17.6)$

CH_3-: $3(0.55 \pm 0.07) = 1.6\ (1.4 - 1.9)$

C=C-H: $(0.01 \pm 0.002) = 0.01\ (0.008 - 0.012)$

$\Sigma = 54\ (21 - 91)$

3-Chloroethylbenzene



ring: $(5 \pm 2)(< 1) = < 5(< 3 - 7)$

$-CH_2-$: $2(2.5 \pm 1) = 5(3 - 7)$

CH_3-: $3(0.065 \pm 0.013) = 0.2(0.16 - 0.23)$

ring-H: $4(0.01 \pm 0.002) = 0.04(0.03 - 0.05)$

$\Sigma = 5\text{-}10(3 - 14)$

FIGURE 5.3 ESTIMATION OF k_{OH} (10^{12} cm^3 molec^{-1} s^{-1}) USING EQUATION AND DATA IN TABLES 5.4 TO 5.6

$$t_{1/2}^{OH}\text{(days)} = 8.0 \times 10^{-12}/k_{OH} \qquad (5.4b)$$

Because [OH] does vary considerably during the day, very reactive compounds ($t_{1/2}^{OH}$ < 0.5 days) will show a range of $t_{1/2}$ values depending on the time of release. However considering that release occurs continually throughout the day, equations (5.4a) and (5.4b) still give the average half-life. The expression will apply best for compounds having $t_{1/2}$ value of 1 to 10 days. For more reactive compounds emitted during the day in polluted areas, the $t_{1/2}^{OH}$ values estimated from equations (5.4a) and (5.4b) will be too large by a factor of 3-10. For compounds of low reactivity where mixing into the entire troposphere occurs, calculated $t_{1/2}^{OH}$ values [equations (5.4a) and (5.4b)] will be a factor of 2-3 too small because of the smaller [OH] at higher elevations (see Section 5.7.4).

5.5.3 Screening Test for Reaction with Ozone

To screen for the importance of reaction with ozone, the structure of the compound is analyzed for the reactive groups identified in Table 5.7. Thus, the method involves determining if the compound has a carbon-carbon double bond; if it does have such a bond, the degree of substitution is determined. Then, from data in Table 5.7, the rate constant for that specific type of group is determined. If the compound contains an aromatic ring, the degree of substitution is determined and the estimated rate constant is determined from Table 5.7. If the molecule contains more than one reactivity group, the molecular reactivity is the sum of the rate constant for each group.

The half-life for reaction with O_3 is

$$t_{1/2}^{O_3} = \ln 2/k_{O_3}[O_3] \qquad (5.5)$$

Since the average tropospheric ozone concentration is 1×10^{12} molec cm^{-3} (1.7×10^{-9} M or 0.041 ppm), the half-life may be expressed as follows:

$$t_{1/2}^{O_3}\text{(seconds)} = 6.9 \times 10^{-13}/k_{O_3} \qquad (5.5a)$$

$$t_{1/2}^{O_3}\text{(days)} = 8.0 \times 10^{-18}/k_{O_3} \qquad (5.5b)$$

where k_{O_3} is in molar units of cm^3 mole^{-1} s^{-1}.

One must keep in mind that ground level ozone concentrations do fluctuate and the true $t_{1/2}$ values will also. In urban atmosphere and downwind from urban centers, the values of daytime ozone concentrations can be 2-5 times larger than used in equations (5.5a) and (5.5b). Therefore the actual $t_{1/2}$ values for reactive compounds ($t_{1/2}$ < 0.5 day) under these conditions will be shorter than estimated by equations (5.5a) and (5.5b) by a similar factor.

TABLE 5.7. RATE CONSTANTS FOR REACTION OF OZONE WITH GENERALIZED STRUCTURES[a]

Structure	10^{18} k_{O_3}, c^3 molec^{-1} s^{-1}	$t_{1/2}$, days
Ethenes	1.9	4.2
alkyl	12	0.7
1,1-dialkyl	14	0.6
1,2-dialkyl		
cis-	160	0.06
trans-	260	0.03
trialkyl	500	0.01
tetraalkyl	1500	0.006
Cycloalkenes		
C_5	800	0.01
C_6	170	0.05
Alkadienes		
1,3-butadiene	8.4	1.0
Benzene	0.00005	2×10^5
alkyl	0.003 - 0.0006	2×10^4
dialkyl	0.001 - 0.002	7×10^3
trialkyl	0.006 - 0.008	2×10^3
tetraalkyl	0.02	400
hexaalkyl	0.4	20
hydroxy	1-2	3-7

[a] Data from Table 5.14.

5.6 DETAILED TESTS

The purpose of the detailed procedures is to determine the rate constants of the chemical processes that control the lifetime of chemicals in the atmosphere. In general, the rate constants need be determined only for processes shown to be of potential importance in the screening tests. Thus if the value of either $t_{1/2}^{OH}$ or $t_{1/2}^{O_3}$ is less than 0.01 times $\bar{t}_{1/2}^{P}$, then only k_{OH} and/or k_{O_3} must be determined. If $\bar{t}_{1/2}^{P}$ is less than 0.01 $t_{1/2}^{OH}$ or $t_{1/2}^{O_3}$, then ϕ and k_p should be determined first, and if $t_{1/2}^{P}$ is less than 0.01 $t_{1/2}^{OH}$ or $t_{1/2}$, then k_{OH} and k_{O_3} need not be measured.

5.6.1 Determination of Quantum Yield for Photolysis

The following equipment is required for measuring the quantum yield for photolysis:

(1) An optical train with the appropriately isolated wavelength of uv or visible light as discussed in Section 5.7.5.

(2) A uv reaction cell, with borosilicate windows if radiation is > 300 nm, or Vycor if radiation is > 220 nm, and a gas handling system such as in Figure 5.2 to handle and measure the pressure of vapor in the cell. No mercury vapor should be allowed in the system because even traces can serve to sensitize photochemical reactions.

(3) An actinometer that photolyzes at the wavelength at which the quantum yield is being measured.

Three sets of experiments are necessary to determine the desired quantum yield. First, tests must be made for a constant rate of photolysis of the actinometer by charging the system with the actinometer, using the technique described in Section 5.5.1 (keeping the absorbance below 0.02). Once the lamp has stabilized, the actinometer must be photolyzed in the optical train until the reaction proceeds to about 10%. Then the process is repeated twice more for two and four times longer. The log of the observed concentration is then plotted versus time. The slope of the regression line (k'_{pa}) is $\alpha_\lambda \ell I_{0\lambda}$. If the plot of the initial and three final concentrations gives no evidence of curvature, the reproducibility of the actinometer and light source have been demonstrated. If the rate of reaction increases with time, then possibly the light source has not been allowed to stabilize sufficiently. If the long run indicates a significantly smaller rate than the shorter runs, then the conversion of the actinometer may be too large (absorbance greater than 0.02) or products are affecting the reaction. Based on these experiments, an optimum time for measuring the light flux can be determined.

In the second set of experiments, the reaction cell is loaded with a pressure of compound not greater than 50% of the room temperature vapor pressure, while keeping the absorbance below 0.02. Then the compound is photolyzed to about 10% conversion. Then two additional runs are made for two and four times longer, always allowing the lamp to stabilize before beginning the reaction. The log of the concentration is plotted at each time, including the initial time, and the regression slope (k'_{pc}) is determined. If the plot shows a noticeable curvature suggesting a slower rate at the later stages, then one of the products may be quenching the reaction; if the curvature suggests a faster rate, then a product may be sensitizing the reaction. In either case, the initial slope would give the most reliable value of k'_{pc}.

If no measurable decomposition can be observed during a reaction time of one week, then the third set of experiments may be omitted and an estimate of a maximum value of the quantum yield can be made from equation (5.9), assuming a loss of an amount equal to twice the standard deviation of the analytical procedure over the maximum reaction time.

From the above experiments, the optimum conditions may be selected for measuring the light flux and photolyzing the compound under study. A third series of experiments should then be carried out consisting of an actinometer run, a sample run, and a second actinometer run using these optimum conditions. From each experiment, an apparent first-order rate constant k'_p is defined. The average of the two actinometer runs (k'_{pa}) is used to determine the light flux for the sample photolysis and thus correct for lamp aging during the experiment. The quantum yield (ϕ_c) can then be calculated from k'_{pa}, the sample constant k'_{pc}, cross sections of compound (σ_c) and actinometer (σ_a), and the actinometer quantum yield (ϕ_a), using the following equation:

$$\phi_c = \phi_a \frac{k'_{pc}}{k'_{pa}} \frac{\sigma_a}{\sigma_c} \qquad (5.6)$$

The process should then be repeated twice, and the average of the three values and the standard deviation should be determined.

The quantum yield may now be combined with the absorbance data using the hand integration data in Section 5.7 to calculate the atmospheric photolysis rate constants at various times of the year and latitudes

$$k_p = \phi_a \Sigma \alpha_\lambda J'_\lambda .$$

If the values of $\bar{k}_p$ have been determined for all the desired times of year and latitude, then k_p is determined by

$$k_p = \phi \bar{k}_p \qquad (5.7)$$

for each case. The half-life is then

$$t_{\frac{1}{2}}(\text{seconds}) = \ln 2/k_p \qquad (5.7a)$$

$$t_{\frac{1}{2}}(\text{days}) = 8.0 \times 10^{-6}/k_p \qquad (5.7b)$$

Error Analysis for k'_p

The estimate of the experimental rate constant k'_p is related to the measured variables, concentration and time, by the following regression equation.

$$k'_p = \frac{n\Sigma t \ln C - [\Sigma t][\Sigma \ln C]}{n\Sigma t^2 - [\Sigma t]^2} \qquad (5.8)$$

where C is concentration of chemical measured at time t. This version of the regression equation does not require that $\ln(C/C_o) = 0$ at $t = 0$; that is, the line is not forced through the origin and any significant departure from the origin indicates bias in values of C at $t > 0$.

The intercept, C_o the concentration at $t = 0$, is obtained from the equation

$$\ln(C_o) = \frac{1}{n}\Sigma \ln C - k_p'(\frac{1}{n}\Sigma t) \qquad (5.9)$$

The preferred measure of error in experiments of this kind is the standard error, σ.* The standard error in k_p' from n measurements where $n > 2$ is given by

$$\sigma^2 = \frac{1}{n - 2}\left[\frac{n\Sigma[\ln C]^2 - [\Sigma \ln C]^2}{n\Sigma t^2 - (\Sigma t)^2} - (k_p')^2\right] \qquad (5.10)$$

Equation (5.13) shows that σ varies approximately with $\frac{1}{\sqrt{n}}$ and directly with $\sigma(C)$.

Error Analysis for ϕ

The equation used to calculate the reaction quantum yield for photolysis of a chemical is

$$\phi_c = \frac{k'_{pc}}{k'_{pa}} \cdot \frac{\sigma_{\lambda a}}{\sigma_{\lambda c}} \cdot \phi_a \qquad (5.11)$$

The standard error may be expressed

$$\frac{\sigma(\phi_c)}{\phi_c} = \left[\frac{\sigma^2(k'_{pc})}{(k'_{pc})^2} + \frac{\sigma^2(k'_{pa})}{(k'_{pa})^2} + \frac{\sigma^2(\sigma_{\lambda a})}{(\sigma_{\lambda a})^2} + \frac{\sigma^2(\sigma_{\lambda c})}{(\sigma_{\lambda c})^2} + \frac{\sigma^2(\phi_a)}{(\phi_a)^2}\right]^{\frac{1}{2}} \qquad (5.12)$$

Thus, if the standard errors for k'_{pc}, k'_{pa}, σ_s, σ_a, and ϕ_s are 0.10, 0.10, 0.05, 0.05, and 0.1, then

$$\frac{\sigma(\phi_c)}{\phi_c} = [(0.10)^2 + (0.10)^2 + (0.05)^2 + (0.05)^2 + (0.1)^2]^{\frac{1}{2}}$$
$$= 0.19$$

---

*The standard error may be expressed as the standard deviation, $k \pm \sigma$; the error ratio, σ/k; or percent error $(\sigma/k) \times 100$.

Error Analysis for k_p

The sunlight photolysis rate constant k_p is calculated from

$$k_p = \phi \Sigma \sigma_\lambda J_\lambda' \tag{5.13}$$

The standard error ratio for k_p is then

$$\frac{\sigma(k_p)}{(k_p)} = \left[\frac{\sigma^2(\phi)}{(\phi)^2} + \frac{\sigma^2 \Sigma \sigma_\lambda J_\lambda'}{(\Sigma \sigma_\lambda J_\lambda')^2}\right]^{\frac{1}{2}}$$

$$= \left[\frac{\sigma^2(\phi)}{(\phi)^2} + \frac{\Sigma \sigma^2(\sigma_\lambda J_\lambda')}{(\Sigma \sigma_\lambda J_\lambda')^2}\right]^{\frac{1}{2}} \tag{5.14}$$

where for each interval λ,

$$\frac{\sigma^2(\sigma_\lambda J_\lambda')}{(\sigma_\lambda J_\lambda')^2} = \frac{\sigma^2(\sigma_\lambda)}{(\sigma_\lambda)^2} + \frac{\sigma^2(J_\lambda')}{(J_\lambda')^2} \tag{5.15}$$

The second term in equation (5.14) can be substituted by the terms in equation (5.15) where, if we assume the standard error ratio in σ_λ is ± 0.04 and in J_λ ± 0.10, then

$$\frac{\sigma^2(\sigma_\lambda J_\lambda')}{(\sigma_\lambda J_\lambda')^2} = [(0.04)^2 + (0.10)^2] = 0.0116$$

and

$$\sigma^2(\sigma_\lambda J_\lambda') = 0.0116(\sigma_\lambda J_\lambda')^2$$

Substitution of error ratios for ϕ and $\sigma_\lambda L_\lambda$ in equation (5.14) then gives

$$\frac{\sigma^2(k_p)}{(k_p)^2} = 0.0116\left[1 + \frac{\Sigma(\sigma_\lambda J_\lambda')^2}{(\Sigma \sigma_\lambda J_\lambda')^2}\right]$$

Multiplication of the last term by ϕ^2/ϕ^2 and substitution of $k_p{}^2$ for $\phi^2(\Sigma\sigma_\lambda J_\lambda')^2$ gives

$$\frac{\sigma(k_p)}{k_p} = 0.108\left\{1 + \frac{\phi^2 \Sigma(\sigma_\lambda J_\lambda')^2}{k_p}\right\}^{\frac{1}{2}} \geq 0.108$$

5.6.2 Determination of Hydroxyl Radical Rate Constant Measurements

Materials needed to determine the hydroxyl radical rate constant include:

(1) Sealed Teflon-film bag of approximately 100-liter volume with fitting to fill and withdraw gas samples.
(2) Pure air source.
(3) Nitrous acid generator consisting of a 500-cc round-bottomed flask with connections to allow the contents to be swept with air. The nitrous acid is generated by adding dropwise a specific amount of an accurately prepared solution of about 5 x 10^{-2}N $NaNO_2$ solution to approximately 150 cc of 5% sulfuric acid under a stream of pure air, which carries the HONO into the reaction bag. (1.0 cc of 5 x 10^{-2}N $NaNO_2$ produces 12.5 ppm HONO in a 100-liter reaction bag if the HONO is completely transferred and none is lost to secondary reactions.)
(4) Appropriate reference compound listed in Table 5.8.

The following procedure is recommended for determining the hydroxyl radical rate constant. The reaction bag is first tested for contamination by filling it with dry air and exposing it to sunlight for one hour. Then air samples are withdrawn and analyzed, using the same analytical conditions to be used to analyze the reaction mixtures. If any substances that will interfere with the analyses are found, then the bag should be cleaned by flushing with pure air for an extended period of time with heating up to 80°C if necessary. If this procedure is not effective, then the bag should be replaced with a bag demonstrated to be uncontaminated with interfering substances.

The uncontaminated bag is filled approximately three-quarters with clean air and then injected with 4-μℓ liquid consisting of each of the compounds to be tested and the reference compound, which is selected to have a reactivity similar to the test compound. The contents of the bag are then mixed by alternately pushing in the sides and ends of the bag several times. At the point of injection, the surface must be inspected to ensure complete volatilization of the reactants. After the bag is allowed to stand for 10-15 minutes, a gas sample is withdrawn and analyzed to serve as an initial reference point. One hour later, a second sample is withdrawn and analyzed. These two analyses should give the same concentrations of each material within the precision of the analytical procedure. If not, additional mixing time is probably needed to complete mixing. Samples should be taken periodically until the analyses are stable. If the analyses show one or both reactants to decrease with time then adsorption on the surface of the bag is occurring; in this case the experiment should be repeated with lower concentrations of substrate.

Once the concentrations of compound and reference are shown to be stable in the reaction bag, approximately 5 x 10^{-2} mmole HONO is generated in the HONO generator while it is swept with pure air to carry the HONO into the reaction bag. Exposure to light is kept to a minimum. The bag is again kneaded to effect complete mixing. After 10 minutes, three samples are withdrawn and analyzed to serve as t_0 points. The bag is then placed outside in the direct sunlight. Under weather conditions that limit the amount of sunlight, the bag may be irradiated by placing it immediately adjacent and parallel to a bank

Table 5.8

REFERENCE COMPOUNDS FOR DETERMINING THE REACTIVITY OF COMPOUNDS TOWARD OH IN THE ATMOSPHERE

Standard Compounds	k_{OH}^{298}, $cm^3 molec^{-1} s^{-1}$	$k_{OH}/k_{OH}^{Methane}$
Methane[a]	9.5×10^{-15}	1.0
1,1,1-Trichloroethane[b]	15.0×10^{-15}	1.6
Chloroform[c] (Trichloromethane)	1.0×10^{-13}	10.5
Ethane[a]	2.9×10^{-13}	30.5
Benzene[d]	1.2×10^{-12}	130
Toluene[d]	6.4×10^{-12}	670
Ethylbenzene[e]	7.9×10^{-12}	1000
m-Xylene[e]	20.6×10^{-12}	2920
2-Methylbutene[f]	80×10^{-12}	10,000

[a] Howard and Evenson, 1976.

[b] Howard and Evenson, 1976 (b).

[c] Howard and Evenson, 1976 (a).

[d] Perry, Atkinson, and Pitts, 1927.

[e] Ravishankara et al. (1978).

[f] Atkinson, ∿1976 or later.

of four to eight standard fluorescent lights. Samples are withdrawn every one-half hour for 4 hours in triplicate and analyzed. In direct sunlight most of the change should have occurred in the first 2 hours; however, in cases where fluorescent lights are used, the conversions are less readily predicted and considerably more time may be required to complete the conversion.

It is important that the conversion of both compound and reference is sufficient. The analyses will fall into four different categories:

(1) If less than 10% change is observed in the compound (assuming a standard deviation for the chemical analysis of 5.0%) and the reference decreases more than 30%, then the experiment should be repeated using a less reactive reference [also see category (3)].
(2) If no change is observed in the standard but the compound decreases (> 30%), then the experiment should be repeated using a more reactive reference.
(3) If neither compound or reference decreases more than 30%, then the experiment should be repeated using 2 to 4 times the amount of HONO.
(4) If both compound and reference decrease more than 30%, then it should be possible to calculate the relative reactivity of compound versus reference as indicated below.

The preferred method of determining the ratio of rate constants for the reaction of compound and standard toward OH radical (k^C_{OH}/k^S_{OH}) is to apply the following expression:

$$\log(C_o/C_t) = (k^C_{OH}/k^S_{OH})\log(S_o/S_t) \qquad (5.16)$$

The ratio of rate constants is the slope when $\log(C_o/C_t)$ is plotted versus $\log(S_o/S_t)$ and can be determined by standard regression methods. If only initial and final points are available, then the ratio of rate constants may be determined directly from the expression

$$\log(C_o/C_t)/\log(S_o/S_t) = k^C_{OH}/k^S_{OH} \qquad (5.16a)$$

The values from each run should be averaged to give the best estimate of k^C_{OH}/k^S_{OH} and standard deviation. In cases where $k^C_{OH}/k^S_{OH} \geq 3$ or ≤ 0.3, data should be carefully analyzed to ensure that the substrate changing the least is changing significantly. (This is especially true if the standard deviation of the individual chemical analyses is greater than 0.05.)

Since k^S_{OH} is available in Table 5.8, k^C_{OH} may be estimated as follows:

$$k^C_{OH} = (k^C_{OH}/k^S_{OH})\cdot k^S_{OH} \qquad (5.17)$$

To verify k^C_{OH}, it is important to repeat the above process with a second standard. This standard should be selected from Table 5.8 to best match k^C_{OH}

as estimated above. For example, if the data indicate k^{C}_{OH} is 5 x $k^{benzene}_{OH}$, then ethylbenzene should be used in the verification.

The environmental half-life is

$$t_{\frac{1}{2}} = \ln 2/k_{OH}[OH] \qquad (5.18)$$

assuming [OH] = 10^{6} molec cc^{-1} (Section 5.7.4),

$$t^{OH}_{\frac{1}{2}}(\text{seconds}) = 6.9 \times 10^{-7}/k_{OH} \qquad (5.18a)$$

$$t^{OH}_{\frac{1}{2}}(\text{days}) = 8.0 \times 10^{-12}/k_{OH} \qquad (5.18b)$$

Error Analysis for Rate Constant Ratio k^{C}_{OH}/k^{S}_{OH}

The estimate of the rate constant ratio k^{C}_{OH}/k^{S}_{OH} in the case of three or more data points is related to the measured concentrations of compound C and reference S_x by the following regression equation:

$$k^{C}_{OH}/k^{S}_{OH} = \frac{n\Sigma\ln(C_o/C_t)\ln(S_o/S_t) - \Sigma\ln(C_o/C_t)\Sigma\ln(S_o/C_t)}{n\Sigma[\ln(S_o/S_t)]^{2} - [\Sigma\ln(S_o/S_t)]^{2}} \qquad (5.19)$$

The best estimate of the standard error is given by

$$\sigma^{2}(k^{C}_{OH}/k^{S}_{OH}) = \frac{1}{n-2}\left[\frac{n\Sigma[\ln(C_o/C_t)]^{2} - [\Sigma\ln(C_o/C_t)]^{2}}{n\Sigma[\ln(S_o/S_t)]^{2} - [\Sigma\ln(S_o/S_t)]^{2}} - (k^{C}_{OH}/k^{S}_{OH})^{2}\right] \qquad (5.20)$$

The value of $\ln(C_o/C_t)$ at $\ln(S_o/S_t) = 0$ may be estimated from the equation

$$\ln(C_o/C_t)_o = \frac{1}{n}\Sigma\ln(C_o/C_t) - \frac{1}{n}(k^{C}_{OH}/k^{S}_{OH})\Sigma\ln(S_o/S_t) \qquad (5.21)$$

The standard error of $\ln(C_o/C_t)$ is

$$\sigma[\ln(C_o/C_t)] = \frac{1}{n^{\frac{1}{2}}(n-1)^{\frac{1}{2}}}[n\Sigma[\ln(C_o/C_t)]^{2} - [\Sigma\ln(C_o/C_t)]^{2}]^{\frac{1}{2}} \qquad (5.22)$$

Since initially $\ln(C_o/C_t)$ is zero, large deviation of the estimated value from zero indicates error in the experimental or statistical procedures.

In cases where only the initial and final concentrations of C and S are measured, the value of k^{C}_{OH}/k^{S}_{OH} is approximated by equation (5.16a). A detailed derivation is given in Appendix 5-A, which indicates this formula has a small bias provided $\ln(S_o/S_t) > \sim 7\sigma_s$. The standard error ratio for k_{OH}/k^{S}_{OH} estimated by this method is expressed as

$$\frac{\sigma(k^C_{OH}/k^S_{OH})}{k^C_{OH}/k^S_{OH}} = \left[\frac{2\sigma^2(\ln C)}{\ln(C_o/C_t)} + \frac{2\sigma^2(\ln S)}{\ln(S_o/S_t)}\right]^{\frac{1}{2}} \qquad (5.23)$$

If $\sigma(\ln C) = \sigma(\ln S) = 0.05$ and $C_o/C_t = S_o/S_t = 2$, then the standard error equals 0.12. However if the conversion of C and S are only 10%, then the standard error is 0.31. Thus, this expression can be very useful for estimating the uncertainty of a result based on the conversion and experimental error in the concentration measurements, and it may be used to select optimum conversions for determining k^C_{OH}/k^S_{OH} by both methods.

5.6.3 Determination of Ozone Reaction Rate Constant Measurement

The following equipment is needed to determine the rate constant for reaction of ozone:

(1) Commercial ozone monitor or comparable assembled system. If such instrumentation is not available, a suitable wet method for determining ozone may be used, such as suggested in the Federal Register (Vol. 43, 26962, June 22, 1978) or by Flamm (1977).

(2) Ozone generator for producing up to 1.0 ppm O_3 in a pure air gas stream.

(3) Two 100-liter Teflon bags. One bag, for containing the reaction, is fitted with a suitable manifold to add the ozone-air mixture and the compound-air mixture, and to withdraw samples for analysis. The volume of the reaction bag is determined to within 5% using a wet test meter. The second bag is used to prepare a mixture of the compound to be studied and is connected to the first by a 10-mm stopcock.

The following procedure is recommended. First, the bag is filled with pure air containing about 1 ppm of O_3 to determine the stability of ozone in the reaction bag. The bag is allowed to stand for one hour in the absence of direct illumination and the ozone is monitored. A plot of the log of the ozone concentration as a function of time is then made. The slope gives the background ozone disappearance rate constant (k_B)

$$\ln(C_o/C_t) = k_B t \qquad (5.24)$$

where C_o and C_t are the concentrations of ozone initially and at time t (in seconds). If k_B is > 0.01 min^{-1}, the bag may be contaminated, in which case the bag should be allowed to stand overnight with ∿ 1 ppm O_3. This treatment should be repeated until the background rate reaches the indicated limit.

Then the reaction bag is filled three-quarters with 1 ppm O_3 in pure air and the ozone concentration is monitored. In the second bag, which should be connected to the first bag with a freshly cleaned 10-mm stopcock, the compound-air mixture is prepared by injecting a sufficient amount of liquid compound to give 20 ppm in 50 liters. (This will give ∿ 7 ppm of compound in the 150-liter reaction bag.) The syringe should be weighed before and after injection to obtain an accurate measure of the amount injected. The bag is mixed by alternately pushing in the sides and ends for several minutes, and is then inspected to ensure no liquid is visible at the place of injection. Once the compound is totally vaporized, the stopcock is opened and the mixture is forced totally (> 95%) into the reaction bag. It may be necessary to vent some of the ozone mixture before adding the hydrocarbon to ensure sufficient space in the reaction bag. Once the hydrocarbon mixture is added, pure air should be added to bring the bag up to volume. There will be a reduction in the ozone reading reflecting the dilution that has occurred.

The rate constant for oxidation by ozone, k_{O_3}, is defined by the relation

$$\ln(C_o/C_t) = (k_B + k_{O_3}[RH])t \qquad (5.25)$$

where C_o and C_t are ozone concentrations at times zero and t, and k_B is the background loss rate constant determined initially. By applying the regression analysis procedure indicated in equation (5.26) below, we obtain the term $k_B + k_{O_3}[RH]$. The rate constant k_{O_3} is then evaluated using the relation

$$k_{O_3} = \frac{(\text{slope}-k_B) \times \text{Molec. Wt.} \times \text{Vol.}}{\text{Weight} \times 6.023 \times 10^{20}} \qquad (5.26)$$

where Weight is the weight of the compound in grams, Molec. Wt. is the molecular weight of the compound, and Vol. is the volume in liters of the reaction bag.

The measurement of k_{O_3} should be repeated several times so as to improve the conditions, increase the accuracy of measurement, and test the dependence on [RH], which should be varied by a factor of 3 at least. If less than 50% of the ozone disappears during the experiment, then additional experiments should be made at higher [RH]. If the total ozone disappears in less than an hour, then the [RH] should be decreased. However, it is important to keep the ratio of $[RH]/[O_3] \geq 10$ if at all possible; therefore, if [RH] is reduced, the initial $[O_3]$ should also be reduced accordingly. The following data should be reported: (1) 5 to 7 values of k_{O_3}, (2) initial concentrations of O_3 and [RH], (3) reactor temperature during each measurement, (4) the average of the k_{O_3} values and the standard deviation.

The half-life is estimated from the expression

$$t_{1/2} = \ln2/k_{O_3}[O_3] \qquad (5.27)$$

Assuming an environmental $[O_3]$ of 1.0×10^{12} molec/cc (= 0.04 ppm) (see Section 5.7.4), this expression reduces to

$$t_{1/2}\text{ (seconds)} = 6.9 \times 10^{-13}/k_{O_3} \qquad (5.27a)$$

$$t_{1/2}\text{ (days)} = 8.0 \times 10^{-18}/k_{O_3} \qquad (5.27b)$$

Error Analysis for k_B and O_3

The estimates of the rate constants k_B and $k_B + k_{O_3}[RH]$ are related to the measured variables, concentration and time, by the following regression equations

$$k_B = \frac{n\Sigma t \ln C - [\Sigma t][\Sigma \ln C]}{n\Sigma t^2 - [\Sigma t]^2} \text{ in the absence of RH} \qquad (5.28)$$

$$k_B + k_{O_3}[RH] = \frac{n\Sigma \ln C - [\Sigma t][\Sigma \ln C]}{n\Sigma t^2 \quad [\Sigma t]^2} \text{ in the presence of RH} \qquad (5.29)$$

where C is concentration of chemical measured at time t. This version of the regression equation does not require that $\ln(C/C_0) = 0$ at $t = 0$; that is, the line is not forced through the origin and any significant departure from the origin indicates bias in values of C at $t > 0$.

The intercept, C_o, the concentration at $t = 0$, is obtained from the equation

$$\ln(C_o) = \frac{1}{n}\Sigma \ln C - k_p\left(\frac{1}{n}\Sigma t\right) \qquad (5.30)$$

The preferred measure of error in experiments of this kind is the standard error, σ. The standard error in k_B and $k_B + k_{O_3}[RH]$ from n measurements is given by

$$\sigma^2 = \frac{1}{n-2}\left[\frac{n\Sigma[\ln C]^2 - [\Sigma \ln C]^2}{n\Sigma t^2 - (\Sigma t)^2} - (k)^2\right] \qquad (5.31)$$

where k is k_B or $(k_B + k_{O_3}[RH])$ depending on the experiment. Equation (5.31) shows that σ varies approximately with $\frac{1}{\sqrt{n}}$ and directly with $\sigma(C)$.

5.7 BACKGROUND

5.7.1 General Considerations

The detailed atmospheric chemistry by which compounds containing carbon- and hydrogen are largely converted to CO_2 and H_2O and by which organic nitrogen and sulfur are converted to nitrates and sulfates is quite complex (Leighton, 1961; Demerjian et al., 1974; Pitts and Finlayson, 1975; Baldwin et al., 1977; Hendry et al., 1978; Carter et al., 1978). We have spent considerable effort studying these processes, and our understanding is reasonably good, although semi-quantitative at best. Currently we are developing chemical mechanisms that describe the chemistry of individual hydrocarbons; the mechanisms, which can be readily integrated as a function of time by numerical methods, are then used to simulate the chemistry occurring in smog chambers for those hydrocarbons. These simulations are reasonably effective in predicting the smog chamber results. However, extrapolating these results to a wide variety of chemical structures under atmospheric conditions introduces uncertainties because in most cases the concentrations of organic compounds and NO_x in the atmosphere are orders of magnitude less than those in the chamber.

Our understanding of atmospheric chemistry is sufficient to allow identification of the critical chemical processes that will affect the lifetime of chemicals in the atmosphere. These processes involve photochemical transformations and oxidation reactions similar to those discussed in previous sections concerning water chemistry. For the purposes of the atmospheric chemistry protocol, these two basic processes are defined as follows.

Photochemical transformations are those reactions wherein the compound absorbs solar energy directly to form an electronically excited intermediate that undergoes further reactions by either first-order or second-order processes. In all cases the rate determining step is the absorption of solar energy and follows the relation

$$\text{Rate of Phototransformation} = \phi I_a/h \tag{5.32}$$

where I_a is the light absorbed (in photons $cm^{-2}\ s^{-1}$), h is the depth (in cm) over which the light is absorbed, and ϕ, quantum yield, is the fraction of excited species that give reaction.

Oxidation reactions involve interaction of a compound in its electronic ground stae with a reactive species such as oxygen, ozone, O atom, or OH radical. In this case the rate determining step is the bimolecular reaction of compound and reactive species

$$\text{Rate of Oxidation} = k_{OX}[OX][C] \tag{5.33}$$

where k_{OX} is the rate constant for the process, [OX] is the concentration of reactive species, and [C] is the concentration of chemical.

The clear distinction between phototransformation and oxidation is important in order to accurately predict the rate of each type of process. The factors that control photochemical transformation are absorption coefficients of the compound in the solar region, solar irradiance, and quantum yield. For oxidation processes the controlling factors are rate constants for reaction with each reactive species and the concentrations of the reactive species.

5.7.2 Photochemical Transformation

Rates of Reaction

The rate of photochemical reaction depends on the absorption of solar energy, which is determined by Beer-Lambert law.

$$I_{o\lambda}/I_{\lambda} = e^{\sigma_{\lambda} C \ell} \tag{5.34}$$

where $I_{o\lambda}$ (in photons $cm^{-2}\ sec^{-1}$) is the intensity of incident light at a given wavelength entering a layer of atmosphere, I_{λ} (also in photons $cm^{-2}\ sec^{-1}$) is the intensity of transmitted light, σ_{λ} is the cross section (in cm^2) at wavelength λ, C is the concentration of chemical (in molecules cm^{-3}), and ℓ is the path length of light. The light absorbed by the chemical ($I_{a\lambda}$) is expressed

$$I_{a\lambda} = I_{o\lambda} - I_{\lambda} = I_{o\lambda}(1 - e^{-\sigma C\ell}) \quad (5.35)$$

Except for NO_2 on occasion, the concentrations of light absorbers in the atmosphere are not sufficient to attenuate the light intensity more than a few percent; thus, equation (5.33) may be simplified by substituting the exponential term with the appropriate approximation ($e^x \cong 1-x$ when $x < 0.02$)

$$I_{a\lambda} = I_{o\lambda} - I_{\lambda} = \sigma C\ell I_{o\lambda} \quad (5.36)$$

$I_{o\lambda}$ is a complex function of the direct light from the sun (I_d) and the scatter light (I_s); the path length (ℓ) varies for both of these. For the direct light

$$\ell_d = h \text{ secant } z$$

where h is the depth of the atmospheric layer of interest. For the scattered light, which is assumed to come equally from all portions of the sky, the average path length is a constant i times the depth

$$\ell_s = ih$$

Leighton has demonstrated that i is approximately 2.

Thus, substituting these and I terms in equation (5.36) gives

$$I_{a\lambda} = \sigma C\{I_{d\lambda} h\text{secant } z + I_{s\lambda} ih\} \quad (5.37)$$

To convert $I_{a\lambda}$ into volume units, we divide by the atmospheric depth, h.

$$\frac{I_{a\lambda}}{h} = \sigma_{\lambda} C\{I_{d\lambda} \text{secant } z + I_{s\lambda} i\} \quad (5.38)$$

Leighton defined the term in the parenthesis as the actinic irradiance, J_{λ}

$$J_{\lambda} = \{I_{d\lambda} \text{secant } z + I_{s\lambda} i\}$$

Thus,

$$\frac{I_{a\lambda}}{h} = \sigma_{\lambda} C J_{\lambda} \quad (5.39)$$

The rate of absorption of light by a compound over the entire solar region (290-800 nm) is

$$\frac{I_a}{h} = C\Sigma\sigma_{\lambda} J_{\lambda}$$

The rate of photochemical reaction is

$$\text{Rate} = \phi\frac{I_a}{h} = \phi C\Sigma\sigma x J_\lambda$$

The apparent first-order rate constant (k_p) is thus

$$k_p = \phi\Sigma\sigma_\lambda J_\lambda \tag{5.40}$$

which is conveniently independent of C and h (concentration and depth of the atmospheric layer).

To determine J_λ values, it is necessary to know the solar intensity at the top of the atmosphere, the absorption due to atmospheric ozone and aerosols, the molecular (Rayleigh) scattering, and the aerosol (Mie) scattering. Leighton originally estimated I_λ values based on limited information. However, Peterson (1976, 1977) has recently reanalyzed the problem and has estimated J_λ values using more recent data, and these values have been summarized by Schere and Demerjian (1977). The differences between Leighton's and Peterson's value are not large because of fortuitous compensation in the various data inputs. Leighton assumed the earth to be nonreflective, whereas Peterson assumed 5 to 15% reflection depending on the wavelength. This difference was largely balanced by the solar constants used by Leighton, which were about 9% larger than those now preferred. Currently, the best values of stratospheric ozone are 35% higher than previous assumptions. This difference is balanced by assumptions regarding light scattering by aerosols. Because of lack of data, Leighton assumed that half of the aerosol scattered radiation was directed backward; Peterson based on the radiative transfer model developed by Dave (1972), assigns only a small fraction of actual backscattering. Since the first two and the last two factors each tend to cancel each other, the differences in J_λ values are not large except at the short wavelengths, where new values are much smaller than the older values. For compounds that absorb broadly over the solar spectrum (such as NO_2, which absorbs more or less equally from 300-400 nm), there is very little difference in the calculated values of k_p. However, for compounds that absorb only near 300 nm, the new data indicate k_p values that are 50% smaller.

One of the most important results of Peterson's analysis is an understanding of the effect of elevation on the J_λ values. This effect results from aerosol scattering of light, which causes J_λ values to increase with elevation. The effect is more important at shorter wavelengths at small zenith angles. Table 5.9 summarizes the effect of elevation and zenith angles on the photolysis of NO_2, assuming aerosol loading and distribution typical of the Los Angeles basin.

The NO_2 photolysis rate at 4 km is about 40% larger than at the surface at low zenith angles and 160% at large zenith angles. For compounds that largely absorb largely near 300 nm, the effect will be about twice as large.

The change in J_λ with elevation tends to level off above 4 km because a large fraction of the aerosol is below that elevation. Thus the NO_2 photolysis values at 4 km should be good estimates for higher elevations.

Table 5.9

EFFECT OF ELEVATION ON RATE CONSTANTS (MIN^{-1}) FOR
PHOTOLYSIS OF NO_2 AS A FUNCTION OF SOLAR ZENITH ANGLE
(PETERSON, 1977)

Level	0	10	20	30	40	50	60	70	78	86
Surface	0.579	0.574	0.560	0.535	0.496	0.438	0.352	0.234	0.114	0.025
0.15 km	0.614	0.609	0.596	0.572	0.534	0.477	0.391	0.264	0.133	0.027
0.36 km	0.645	0.640	0.628	0.605	0.568	0.512	0.426	0.295	0.153	0.030
0.64 km	0.675	0.671	0.659	0.637	0.601	0.545	0.459	0.325	0.174	0.034
0.98 km	0.703	0.700	0.688	0.667	0.631	0.576	0.490	0.353	0.194	0.037
1.38 km	0.729	0.725	0.715	0.694	0.659	0.604	0.517	0.378	0.212	0.040
1.84 km	0.752	0.748	0.737	0.717	0.683	0.628	0.541	0.400	0.229	0.043
2.35 km	0.772	0.769	0.758	0.738	0.704	0.650	0.564	0.421	0.246	0.046
2.91 km	0.790	0.787	0.777	0.758	0.725	0.673	0.586	0.443	0.264	0.050
3.53 km	0.808	0.805	0.795	0.776	0.745	0.694	0.608	0.466	0.283	0.055
4.21 km	0.824	0.821	0.812	0.794	0.764	0.713	0.631	0.489	0.303	0.060

When photolysis rates are estimated for compounds that are widely mixed in the troposphere, the surface photochemical reaction rate estimated from ground level J values will be low. In these cases, rates should be increased by about 50% for compounds photolyzing from absorption primarily in the longer wavelength region. Compounds that photolyze in the ∿ 300 nm region will photolyze faster by about a factor of two. Computational techniques are available to more accurately calculate the effect of elevation on the photolysis for any compound; however, they require considerable computational time and the gain in accuracy over these approximations is probably not significant.

Computation of Photochemical Reaction Rates

To calculate the photochemical reaction rate constants, it is necessary to integrate equation (5.39) over the solar spectrum.

$$k_p = \phi \Sigma \sigma_\lambda J_\lambda \qquad (5.41)$$

Schere and Demerjian (1977) have published a computer routine to carry out this integration over 10-mm wavelength intervals. The routine calculates momentary photochemical rate constants throughout the day for any day of the year at any latitude and longitude. The J_λ values of Peterson are used in the calculations. Because most compounds require more than one day to photolyze, it is necessary to integrate the output from the Schere and Demerjian routine to obtain rates on a day basis.

To facilitate the computation of photochemical rate constants, we have prepared in Tables 5.1 to 5.3 day-averaged light intensity values as a function of wavelength at latitudes of 10, 30, and 50°N for the summer and winter solstices and the equinox. In addition, the tables include average rates for spring-summer and fall-winter light intensity values. The light intensity values in the tables refer to J_λ' values and represent that total available actinic light flux in a given wavelength region for a specific day and at a specific latitude. The wavelength ranges in Tables 5.1 to 5.3 are divided into 31 intervals over the total range 290-800 nm to maintain reliability of the calculations and yet to allow them to be carried out rapidly.

The data in Tables 5.1 to 5.3 are multiplied by the average absorption coefficients over the wavelength ranges in the appropriate table with corresponding J_λ' values and summing

$$\bar{k}_p = \Sigma \sigma_\lambda J_\lambda'$$

$$k_p = \phi \Sigma \sigma_\lambda J_\lambda'$$

The value of k_p corresponds to the latitude and time of year of the J_λ' values used.

To test the reliability of the hand calculation procedure, photolysis rates for benzaldehyde and biacetyl were calculated using both these methods and the 10-nm interval computer computation. Both methods gave identical rates within 1%. Table 5.10 summarizes the rates. To demonstrate the hand computation, Table 5.11 shows calculations of the photolysis rates for benzaldehyde and biacetyl.

5.7.3 Atmospheric Oxidation

General

Except for some compounds that photolyze rapidly, the most important reactions of organic compounds in the atmosphere are with OH radical and ozone. Table 5.12 summarizes approximate daytime concentrations of these species along with a number of other oxidants also believed to be present in the atmosphere. Included in the table are rate constants for reaction of these oxidants with propene, n-butane, and toluene, which are common atmospheric pollutants. The product of the rate constant and the concentration of oxidant is the apparent first-order rate constant (k'_{OX}) for that process.

$$\text{Rate} = k_{OX}[OX][C] = k'_{OX}[C]$$

Clearly, in the case for propene the reaction with OH is most important, while the reaction with O_3 is second most important. Together, OH and O_3 account for more than 99% of the reaction; ground state oxygen atom ($O(^3P)$) accounts for only 0.1% of the reaction. For both n-butane and toluene, OH alone accounts for greater than 99% of the reaction. These conclusions obviously are dependent on the concentrations that are assigned for each oxidant. However, the concentrations of OH and O_3 are not expected to vary significantly from the values in the table (see Section 5.7.5).

In some cases a compound might have unusually high reactivity to one of the other oxidants, although this should be the exception. One important case is the oxidation of NO by HOO• (or ROO•). The reaction

$$HOO\bullet + NO \longrightarrow HO\bullet + NO_2 \qquad (5.42)$$

is the major route by which NO is oxidized in the atmosphere. The reaction competes favorably with the reaction with ozone. However, to our knowledge, there are no cases involving organic compounds where reaction with oxidants other than OH and O_3 are important.

Thus, to estimate the lifetime of chemicals in the atmosphere as determined by oxidation processes, we need to determine only the rate constants for reactions with OH and O_3. The rate constants for reaction of a number of compounds with OH and O_3 are summarized in Tables 5.13 and 5.14.

The lifetime(τ) for reaction of substrate (S) with an oxidant is defined as

$$\tau = \frac{[S]}{k_{OX}[OX][S]} = 1/k_{OX}[OX] \qquad (5.43)$$

Table 5.10

RATE CONSTANTS FOR PHOTOLYSIS OF BENZALDEHYDE AND BIACETYL AS A FUNCTION OF LATITUTDE AND DATE[a]

Compound	Date	Rate Constant, days^{-1}		
		10°N	30°N	50°N
Benzaldehyde	June 22	7.91	8.80	8.86
	March 21/ Sept. 23	7.67	6.78	4.90
	Dec. 22	6.25	3.84	1.02
	Spring/ Summer Average	7.89	8.10	7.41
	Fall/ Winter Average	6.76	4.96	2.42
Biacetyl	June 22	9.83	10.9	11.3
	March 21/ Sept. 23	9.49	8.74	6.95
	Dec. 22	8.14	5.54	1.86
	Spring/ Summer Average	9.76	10.1	9.74
	Fall/ Winter Average	8.73	6.73	3.80

[a] Computed by computer routine and data in Tables 5.1 to 5.3; seasonal averages computed only from tables.

Table 5.11

EXAMPLES OF HAND COMPUTATION OF PHOTOCHEMICAL RATE CONSTANTS[c]

	Avg. Cross-Section (σ_λ)	J'_λ, Photon cm^{2}d^{-1}	$\sigma_\lambda J'_\lambda$, d^{-1}	$\Sigma\sigma_\lambda J_\lambda'$, d^{-1}
— Benzaldehyde[a] Day Rates at 30°N on Summer Solstice —				
285-295	7.10 -20	1.0 16	7.10 -4	7.10 -4
295-305	3.33 -20	7.4 17	2.46 -2	2.54 -2
305-315	3.84 -20	1.09 19	4.19 -1	4.44 -1
315-325	4.30 -20	2.74 19	1.18	1.62
325-335	4.22 -20	4.98 19	2.10	3.72
335-345	3.42 -20	5.49 19	1.88	5.60
345-355	2.76 -20	6.28 19	1.73	7.33
355-365	1.32 -20	6.49 19	8.57 -1	8.19
365-375	7.48 -21	8.09 19	6.05 -1	8.80
				$\bar{k}_p$ = 8.80 d^{-1}
— Biacetyl[b] Day Rates at 30°N on Summer Solstice —				
285-295	1.03 -20	1.0 16	1.03 -4	1.03 -4
295-305	4.98 -21	7.4 17	3.69 -3	3.79 -3
305-315	2.04 -21	1.09 19	2.22 -2	2.60 -2
315-325	1.11 -21	2.74 19	3.04 -2	5.64 -2
325-335	9.61 -22	4.98 19	4.79 -2	1.04 -1
335-345	2.19 -21	5.49 19	1.20 -1	2.25 -1
345-355	3.94 -21	6.28 19	2.47 -1	4.72 -1
355-365	6.10 -21	6.49 19	3.96 -1	8.68 -1
365-375	8.68 -21	8.09 19	7.02 -1	1.57
375-385	1.24 -21	7.93 19	9.83 -1	2.55
385-395	1.88 -20	8.12 19	1.53	4.08
395-415	2.37 -20	1.11 20	2.63	6.71
415-435	2.96 -20	1.41 20	4.17	10.88
				$\bar{k}_p$ = 10.88 d^{-1}

[a] Cross-section data from Berger, 1973.

[b] Cross-section data from Calvert and Pitts, 1966.

[c] Second number in column is the power of ten by which the first number is multiplied.

Table 5.12

APPARENT FIRST-ORDER RATE CONSTANTS FOR REACTIONS OF ATMOSPHERIC OXIDANTS WITH PROPENE, n-BUTANE, AND TOLUENE[a]

Oxidant	Concentration[b] (molec cc^{-1})	Propene		n-Butane		Toluene	
		k_{OX}	$k_{OX}[OX]$	k_{OX}	$k_{OX}[OX]$	k_{OX}	$k_{OX}[OX]$
OH	2×10^{6}	2.5×10^{-11}	5×10^{-5}	2.7×10^{-12}	5×10^{-6}	6.4×10^{-12}	1×10^{-5}
O_3	1×10^{12}	1.0×10^{-17}	1×10^{-5}	~ 0	~ 0	~ 0	~ 0
$O(^3P)$	3×10^{4}	3.5×10^{-12}	1×10^{-7}	5.2×10^{-14}	2×10^{-9}	7.5×10^{-14}	2×10^{-9}
$O(^1D)$	2×10^{-1}	$\sim 1 \times 10^{-14}$	2×10^{-12}	$\sim 1 \times 10^{-11}$	2×10^{-12}	$\sim 1 \times 10^{-11}$	2×10^{-12}
$HO_2 \bullet$ ($RO_2 \bullet$)	1×10^{10}	$< 2 \times 10^{-18}$	$< 2 \times 10^{-8}$	~ 0	~ 0	$\sim 1 \times 10^{-18}$	1×10^{-8}
$O_2(^1\Delta_2)$	1×10^{9}	$\leq 1.7 \times 10^{-20}$	$\leq 2 \times 10^{-11}$	~ 0	~ 0	~ 0	~ 0
NO_3	2×10^{8}	5.3×10^{-15}	1×10^{-6}	~ 0	~ 0	~ 0	~ 0

[a] Rate constants from references shown below; concentrations are estimated based on smog chamber stimulation data from Hendry (1978); rate constants were taken from Hampson and Garvin (1978), Hendry and Mabey (1978), Demerjian, Kerr, and Calvert (1974), Japar and Niki (1975).

[b] To convert to ppm multiply by 4.1×10^{-14}; to convert to M, multiply by 1.7×10^{-21}.

Table 5.13

RATE CONSTANTS AND ENVIRONMENTAL HALF-LIVES FOR REACTIONS OF HYDROXYL RADICALS NEAR 300°K[a]

Compound	10^{12} k_{OH}, cm^3 $molec^{-1}$ s^{-1}	$t_{1/2}$, days[b]
Alkanes		
Methane	0.0079	1,000
Ethane	0.29	28
Propane	2.2	3.6
Methyl	2.2	3.6
Dimethyl	0.81	9.9
n-Butane	2.7	3.0
Methyl	3.3	2.4
2,3-Dimethyl	5.1	1.6
2,2,3-Trimethyl	3.8	2.1
2,2,3,3-Tetramethyl	1.1	7.3
n-Pentane	6.5	1.2
2-Methyl	5.3	1.5
3-Methyl	7.1	1.1
2,2,4-Trimethyl	3.8	2.1
n-Hexane	6.0	1.3
n-Octane	8.5	0.9
Cycloalkanes		
c-Butane	1.2	6.7
c-Pentane	6.1	1.3
c-Hexane	7.0	1.1
Haloalkanes		
Methane		
Fluoro-	0.016	500
Difluoro-	0.0078	1,030
Trifluoro-	0.0002	40,000
Tetrafluoro-	< 0.0004	> 20,000
Chloro-	0.04	200
Dichloro-	0.14	57
Trichloro-	0.11	73
Tetrachloro-	< 0.0004	> 20,000
Bromo	0.04	200
Ethane		
Chloro	0.39	20
1,1-Dichloro	0.26	31
1,2-Dichloro	0.22	36
1,1,1-Trichloro	0.015	530
1,1,1-Trifluoro-2-chloro	0.010	800
1,1,1-Trifluoro-2,2-dichloro	0.028	280
1,1,1,2-Tetrafluoro-2-chloro	0.012	670
1,2-Dibromo	0.25	32
Alkanone		
Butanone	3.3	2.4
2-Methylpentanone	14.9	0.54
2,6-Dimehtylheptanone	24.9	0.32
Alkanols		
Methanol	0.95	8.4
Ethanol	3.0	2.7
Propanol	3.8	2.1
2-Propanol	7.1	1.1
Butanol	6.8	1.2
4-Methyl-2-pentanol	7.1	1.1
O,N,S Substituted alkanes		
Methyl ether	3.5	2.3
Ethyl ether	9.3	0.86
n-Propyl ether	17.3	0.46

Table 5.13

RATE CONSTANTS AND ENVIRONMENTAL HALF-LIVES FOR REACTIONS OF HYDROXYL RADICALS NEAR 300°K (Cont.)

Compound	10^{12} k_{OH}, cm^3 $molec^{-1}$ s^{-1}	$t_{½}$, days[b]
O,N,S Substituted alkanes		
Tetrahydrofuran	14.6	0.55
1-Propylacetate	4.5	1.8
2-Butylacetate	5.6	1.4
Methylamine	21.9	0.37
Methyl sulfide	33.9	0.24
Formaldehyde	15	0.53
Acetaldehyde	16	0.50
Propionaldehyde	21	0.38
Benzaldehyde	13	0.61
Alkenes		
Ethene	7.9	1.0
Propene	24.8	0.5
Methyl-	50.6	0.2
1-Butene	35.4	0.3
2-Methyl	58.1	0.2
3,3-Dimethyl	28.2	0.4
2-Butene		
cis-	53.6	0.2
trans-	69.9	0.2
2-Methyl	79.7	0.1
2,3-Dimethyl	153	0.1
1-Pentene	29.9	0.4
cis-2-Pentene	64.8	0.2
1-Hexene	31.5	0.4
1-Heptene	36.5	0.3
Cycloalkenes		
c-Cyclohexene	71.4	0.2
1-Methyl	96.3	0.1
Haloalkenes		
Ethene		
Fluoro	5.6	1.4
1,1-Difluoro	2.0	4.0
Chloro	6.6	1.2
Trichloro	2.0	4.0
Tetrachloro	0.17	47
Chlorotrifluoro	7.0	1.1
Bromo	6.8	1.2
O-Substituted alkene		
Methoxy	33.5	0.24
Alkadienes		
Propadiene	4.5	2.6
1,3-Butadiene	77	0.1
2-Methyl	78	0.1
Terpenes		
p-Menthane	6.6	1.2
α-Pinene	25.7	0.31
β-Pinene	21.6	0.37
3-Carene	28.2	0.28
Carvomenthane	41.5	0.19
β-Phellandrone	38.2	0.21
d-Limonene	48.1	0.17
Dihydromyrcene	59.7	0.13
Myrcene	74.7	0.11
cis-Ocimene	105	0.076

Table 5.13

RATE CONSTANTS AND ENVIRONMENTAL HALF-LIVES FOR REACTIONS OF HYDROXYL RADICALS NEAR 300°K (Conc.)

Compound	10^{12} k_{OH}, cm^3 $molec^{-1}$ s^{-1}	$t_{1/2}$, days[b]
Alkynes		
Ethyne	0.16	50
Methyl	0.95	8.4
Aralkanes		
Benzene	1.4	5.7
Methyl	5.9	1.3
1,2-Dimethyl	13	0.62
1,3-Trimethyl	20	0.40
1,4-Trimethyl	10	0.80
1,2,3-Trimethyl	24.7	0.32
1,2,4-Trimethyl	33.2	0.24
1,3,5-Trimethyl	49.3	0.16
Ethyl	7.5	1.1
1,2-Ethylmethyl	13.6	0.59
1,3-Ethylmethyl	19.4	0.41
1,4-Ethylmethyl	12.9	0.62
propyl	6.0	1.3
2-propyl	7.8	1.0
1,4-methylpropyl-2-	15.2	0.53
hexafluoro	0.22	36
propylpentafluoro	3.0	2.7
Substituted Aralkanes		
Methoxybenzene	19.6	0.41
o-Cresol	34.0	0.24

[a] Compiled from data and references in Pitts et al., 1977, and Hampson and Garvin, 1978.

[b] Environmental half-lives in 24-hour days, assuming an OH concentration equal to 1 x 10^6 radicals cm^{-3}

Table 5.14

RATE CONSTANTS AND ENVIRONMENTAL HALF-LIVES FOR REACTIONS OF OZONE AT 300°K

Compound	10^{18} k_{O_3}, cm^3 $molec^{-1}$ s^{-1}	Reference	$t_{1/2}$, days
Alkanes			
Methane	1.4(-6)	a	5.73 (6)
Ethane	1.2(-6)	b	6.68 (5)
Propane	6.8(-6)	a	1.18 (6)
Methyl	2.0(-6)	a	3.95 (5)
n-Butane	9.8(-6)	a	8.18 (6)
Alkenes			
Ethene	1.9	h	4.22
Propene	13	h	.617
Methyl-	15.1	h	1.30
1-Butene	12.3	h	.652
2-Butene			
cis-	161	h	.05
trans-	260	h	.031
2-Methyl	493	h	.016
2,3-Dimethyl	1510	h	.005
1-Pentene	10.7	h	.75
2-Pentene			
cis-	456	h	.018
trans-	563	h	.014
1-Hexene	11.1	h	.723
1-Heptene	8.14	e	.99
1-Octene	8.14	e	.99
1-Decene	1.08	e	7.43
Cyclohexene	169	h	.047
Conjugated Alkenes			
1,3-Butadiene	8.4	h	.95
Phenylethene	171.0	i	.05

Table 5.14

RATE CONSTANTS AND ENVIRONMENTAL HALF-LIVES FOR REACTIONS OF OZONE AT 300°K
(Continued)

Compound	10^{18} k_{O_3}, cm^3 $molec^{-1}$ s^{-1}	Reference	$t_{1/2}$, days
Halogenated Alkenes			
Ethene			
Chloro	1.96	i	4.09
1,1-Dichloro	3.67 (-2)	i	2.19 (2)
1,2-Dichloro			
cis	6.14 (-2)	g	1.31 (2)
trans	3.82 (-1)	g	2.10 (1)
Trichloro	5.98 (-3)	i	1.34 (3)
Tetrachloro	1.66 (-3)	i	4.83 (3)
Tetrafluoro	134	c	.06
Propene			
3-Chloro	18.3	i	.438
Hexafluoro	21.6	c	.37
Terpenes			
α-Pinene	164	d	.05
Alkynes			
Ethyne	7.8 (-2)	j	102.8
Aromatic Hydrocarbons			
Benzene	4.65 (-5)	f	1.72 (5)
Methyl	2.76 (-4)	f	2.91 (4)
1,2-Dimethyl	1.58 (-3)	f	5.09 (3)
1,3-Dimethyl	1.30 (-3)	f	6.19 (3)
1,4-Dimethyl	1.58 (-3)	f	5.09 (3)
1,3,4-Trimethyl	4.65 (-3)	f	1.76 (3)
1,3,5-Trimethyl	6.97 (-3)	f	1.15 (3)
1,2,4,5-Tetramethyl	1.78 (-2)	f	4.51 (2)
Pentamethyl	8.30 (-2)	f	96.6
Hexamethyl	0.407	f	19.71
Ethyl	5.65 (-4)	f	1.42 (4)

Table 5.14

RATE CONSTANTS AND ENVIRONMENTAL HALF-LIVES FOR REACTIONS OF OZONE AT 300°K
(Concluded)

Compound	$10^{18}\ k_{O_3}$, $cm^3\ molec^{-1}\ s^{-1}$	Reference	$t_{1/2}$, days
Aromatic Hydrocarbons			
Benzene (cont.)			
1,3-Diethyl	1.78 (-3)	f	4.51 (3)
1,3,5-Triethyl	5.64 (-3)	f	1.42 (3)
Pentaethyl	1.74 (-2)	f	4.61 (2)
Hexaethyl	5.58 (-3)	f	1.44 (3)
2-Propyl	5.81 (-4)	f	1.38 (4)
t-Butyl	1.15 (-4)	f	6.97 (4)

[a] Schubert and Pease (1956).
[b] Morrissey and Schubert (1963).
[c] Heicklen (1966).
[d] Ripperton and Jeffries (1972).
[e] Cadle and Schadt (1952).
[f] Nakagawa, Andrews, and Keefer (1960).
[g] Blume, Hisatsune, and Heicklen (1976).
[h] Japar, Wu, and Niki (1974).
[i] Williamson and Cvetanovic (1968).
[j] Cadle and Schadt (1953).

where k_{OX} is the bimolecular rate constant and [OX] is the approximate concentration of the reactive species. The time to deplete one-half of the chemical is referred to as the half-life ($t_{\frac{1}{2}}$) and is defined

$$t_{\frac{1}{2}} = \ln 2/k_{OX}[OX] = \tau \ln 2 \qquad (5.44)$$

Atmospheric Concentration Units

The subject of reaction kinetics is sometimes complicated by the use of different units to express concentrations and rate constants. In this atmospheric protocol we have followed the current practice in gas-phase kinetics of expressing concentration in units of molecules/cm^3 (molec/cm^3). Table 5.15 lists conversion factors for use in converting to other common units of measurement.

Concentrations are often expressed in molar units (moles/liter). As shown in Table 5.15, concentration in molec/cc is interconverted to molar units by a factor of 1.66×10^{21}:

$$(\text{Conc. in molec/cm}^3) \times 1.66 \times 10^{-21} = \text{Conc. in moles/liter}$$

$$(\text{Conc. in moles/liter})/1.66 \times 10^{-21} = \text{Conc. in molec/cm}^3$$

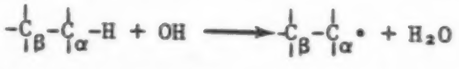
Second-order rate constants depend on the concentration units used to express concentration. Thus, when concentration is expressed in molec/cm^3, the second-order rate constant will be expressed in units of $(\text{molec/cm}^3)^{-1}\,s^{-1}$ or cc/molec-s, which in most cases is the preferred convention for gas-phase rate constants. To convert rate constants expressed in these concentration units to other units, it is necessary to divide by the corresponding factor in Table 5.15 because of the inverse nature of the concentration term in the rate constant units. Thus, to convert a rate constant in cc/molec-s to liters/mole-s (the convention used in solution chemistry), one divides by 1.66×10^{21}.

To convert to the often used units of ppm^{-1} min^{-1}, it is necessary to divide by 4.06×10^{-14} and then multiply by 60 sec/min to change the time unit.

$$(k \text{ in cm}^3/\text{molec-s})\, 1.48 \times 10^{15} = k \text{ in ppm}^{-1}\,\text{min}^{-1}$$

Hydroxyl Radical Reactions and Rates

From the data in Table 5.13 it is possible to make a number of generalizations about OH reactivity that can be useful in estimating the reactivity of compounds. Most alkanes except methane and ethane react toward OH with a rate constant of 1 to 10×10^{-12} cm^{-3} molec s^{-1}. The reaction with alkanes entails abstraction of hydrogen to form water and an alkyl radical



$$-\overset{|}{\underset{|}{C}}_{\beta}-\overset{|}{\underset{|}{C}}_{\alpha}-H + OH \longrightarrow -\overset{|}{\underset{|}{C}}_{\beta}-\overset{|}{\underset{|}{C}}_{\alpha}\bullet + H_2O \qquad (5.45)$$

Substituents can have a number of different effects. Single halogen atoms in

Table 5.15

FACTORS FOR INTERCONVERTING ATMOSPHERIC CONCENTRATION UNITS

(To convert units in first column to units in another column, multiply by number in the column of the desired unit.)

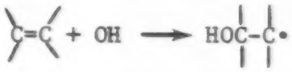
Unit	Molec/cc	atm(25°C)	ppm(25°C)[a]	Moles/ cm^3	Moles/liter
molec/ cm^3	1.0	4.06×10^{-20}	4.06×10^{-14}	1.66×10^{-24}	1.66×10^{-21}
atm(25°C)	2.46×10^{19}	1.0	1.00×10^{6}	4.09×10^{-5}	4.09×10^{-2}
ppm(25°C)[a]	2.46×10^{13}	1.0×10^{-6}	1.0	4.09×10^{-11}	4.09×10^{-8}
moles/ cm^3	6.02×10^{23}	2.44×10^{4}	2.44×10^{10}	1.0	1.00×10^{3}
moles/liter	6.02×10^{20}	24.4	2.44×10^{7}	1.00×10^{-3}	1.0

[a] Assumes total pressure of 1 atm.

the α-position activate the carbon-hydrogen bond but in the β-position they tend to deactivate the bond. Thus, single halogen atoms do not have a large effect on the reactivity of any alkane except methane. Multiple halogens in a molecule generally deactivate the molecule relative to the parent alkane. Thus 1,1,1-trichloroethane is about 1/20 as reactive as ethane; one-half of the reduction is due to reduction of the number of available hydrogens and then each remaining hydrogen is reduced in reactivity by 1/10.

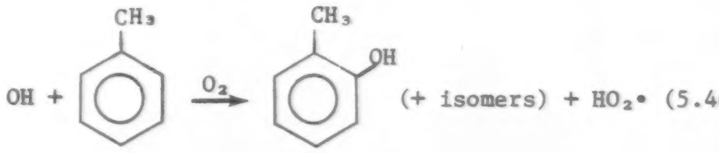
In ketones, alcohols, ethers, and esters, activation is seen relative to the parent hydrocarbon after correction for the number of hydrogens. Amines and sulfide appear to show even larger rate enhancement due to activation of adjacent C-H groups.

The carbon-carbon double bond is much more reactive than the carbon-hydrogen bond and reacts by addition of OH, which generally causes cleavage of the double bond (Niki et al., 1978).



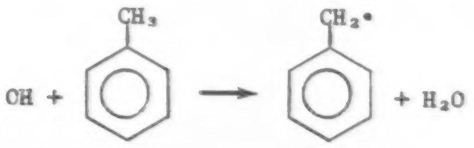
Rate constants for these processes are sensitive to the degree of alkyl substitution on the double bond and vary from 20-200 x 10^{-12}. Consequently, alkenes have a half-life in the environment one-tenth of that for most alkanes. Halogens tend to reduce alkene reactivity somewhat, whereas methoxy has the same effect as an alkyl group. Conjugated dienes have reactivities equal to two double bonds. The reactivities of terpenes are consistent with the similarly substituted alkenes. Alkynes appear to be less reactive than the corresponding alkenes.

Aromatic hydrocarbons have reactivities about the same as alkenes as a result of addition of OH to the ring (Kenley, 1978). For example, 85% of the time, the reaction of toluene with OH gives



(5.46)

Hydrogen abstraction (shown below) occurs only 15% of the time.



(5.47)

For screening studies it is desirable to be able to estimate rate constants for reaction of various kinds of organic structures with OH. A reasonably reliable predictive scheme can be developed on the basis that the rate constant or total molecular reactivity of a molecule is the sum of rate constants for reactivities of each portion of the molecule, and that little or no effect is exerted on the reactivity of a specific site by a substituent more than two atoms away. Thus, the same group in different molecules is assumed to have the same reactivity. For example, the methyl groups in all alkanes are assumed to have the same reactivity; however, methyl groups in compounds like toluene, acetone, and methyl chloride are assumed to have different reactivities because the second atom from the hydrogen, which is abstracted, is different.

The chemistry of OH reactions is largely limited to the three kinds of reactions discussed above: abstraction of a hydrogen atom, addition to a carbon-carbon double bond, and addition to an aromatic ring. These reactions are considered separately in the additivity scheme.

The rate of hydrogen atom abstraction is affected by substitution on the same and adjacent atoms. The total rate constant for abstraction (k_H) may be expressed as the summation of the rate constants for each reactive hydrogen atom

$$k_H = \sum_{i=1}^{i} n_i \alpha_{Hi} \beta_{Hi} k_{Hi} \tag{5.48}$$

where k_{Hi} is the reactivity of the ith hydrogen atom and depends on the degree of substitution on the adjacent atom and on whether a vinyl or phenyl group is attached. The terms α_H and β_H account for the effect of substituents other than hydrogen; α_H is the constant for the substituent in the α-position and β_H is the substituent in the β-position. The term n_i is the number of times the same type of hydrogen group with the same α and β substituents appears in the molecule.

The rate constant for addition to a carbon-carbon double bond (k_E) is expressed by

$$k_E = \sum_{j=1}^{j} \alpha_{E_j} k_{E_j} \tag{5.49}$$

where k_{E_j} is the reactivity of the jth carbon-carbon double bond and depends on the degree of substitution by carbon, oxygen, nitrogen, or sulfur but not halogen. The α_{E_j} term is unity unless a halogen is immediately attached to the double bond.

Similarly, the rate constant for addition to aromatic rings (k_A) is expressed by

$$k_A = \sum_{\ell=1}^{\ell} \alpha_{A\ell} k_{A\ell} \tag{5.50}$$

where $k_{A\ell}$ is the reactivity of the ℓth aromatic group, which depends on the degree of alkyl substitution. The $\alpha_{A\ell}$ is a factor to account for the effect of halogen atoms substituted in the ring.

Thus the total molecular rate constant (k_{OH}) can be expressed by the sum of these three processes

$$k_{OH} = \sum_{i=1}^{i} n_i \alpha_{Hi} \beta_{Hi} k_{Hi} + \sum_{j=1}^{j} \alpha_{E_j} k_{E_j} + \sum_{\ell=1}^{\ell} \alpha_{A\ell} k_{A\ell} \qquad (5.51)$$

The α and β constants in equation 5.51 have been calculated from the data in Table 5.13 and are summarized in Tables 5.4 to 5.6. Figure 5.3 gives the reactivities of four representative compounds. In these examples the uncertainty in the estimated value of k_{OH} is about a factor of 2, the range being one-half the estimate to twice the estimate. Rate constants have been measured for the first two examples and the data are given in the figure. The values are consistent with estimated limits.

Ozone Reactions and Rates

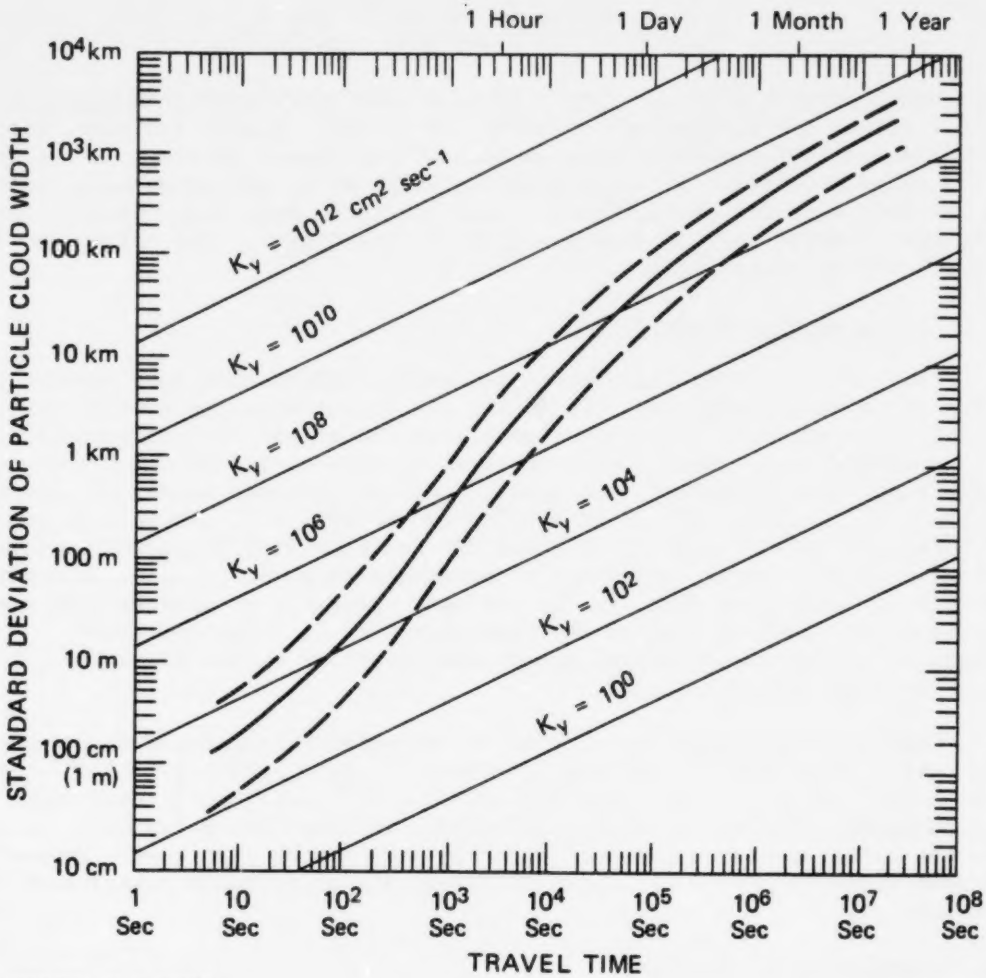
The only organics that react with ozone sufficiently fast for the reaction to be environmentally significant are the alkenes and some of the aromatic hydrocarbons. Table 5.7 summarizes the effect of structure on the rate constants. The substituent increases the reactivity of the carbon-carbon double bond, but the effects are small. Most all alkenes appear to have rate constants in the range of $1.6\text{-}22 \times 10^{-18}$ cm^3 $molec^{-1}$ s^{-1}. These rate constants are about 10^{-7} times larger than those for reaction with OH radical. However, the ratio of the average atmospheric conentrations of ozone to OH is about 10^6 or slightly larger, so that, on the average, reactions of alkenes with ozone are about one-tenth as fast as the reactions with OH. In some cases, because of variations of OH and ozone concentrations in the atmosphere, the ozone reaction may predominate.

The rate constants for reaction of aromatic hydrocarbons with ozone vary over a wide range, from less than 10^{-21} to 10^{-18} cm^{-3} $molec^{-1}$ s^{-1}. Because ozone concentrations range from $0.3\text{-}3 \times 10^{12}$ molec cm^{-3}, only under the most favorable conditions can the half-lives be less than a few days, in which case the ozone reactions compete favorably with the OH reactions. However, for most aromatic compounds, ozone reactions are unimportant relative to OH reactions.

5.7.4 Environmental Studies

Problems of Direct Measurement of Atmospheric Lifetimes

Direct determination of the lifetime of chemicals in the atmosphere is a large-scale undertaking. When chemicals are released to the atmosphere, they are quickly dispersed over large distances and volumes. Turbulent mixing and diffusion cause the chemical to spread in all directions, and winds carry the emissions downwind. The rate of mixing depends on the size of area over which the emission occurs. Figure 5.4 shows the correlation of the diameter of a cloud center core (expressed as one standard deviation or diameter of 2/3 of the mass) with time under ideal conditions. A spherical emission with a diameter of 1 meter doubles in about 10 seconds and is diluted eightfold. After a minute the diameter increases tenfold or to 10 meters, and is diluted



SOURCE: Hage (1965).

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FIGURE 5.4 CLOUD GROWTH AS A FUNCTION OF TIME AND CLOUD SIZE

The growth of the lateral dimensions of plumes and clouds emitted from single sources as a function of residence time in the atmosphere.

The diagonal lines, labeled *K*, indicate cloud growth, assuming a constant diffusivity, K_y, in the relationship $\sigma^2 = KT$. The dashed lines enclose all observations of cloud dimensions.

one thousandfold. Finally after a day the cloud will cover about 100 km and have undergone a dilution of the order of 10^4 to 10^6. Thus, any attempt to follow the decrease of a chemical with an appreciable half-life becomes impossible because of the extreme degree of dilution.

Because of these mixing and transport problems, controlled field studies to measure the environmental lifetime cannot be considered, except possibly in special cases where chemical lifetimes are very short (less than one hour) or where there are unique emissions of chemical already present. Instead, it is necessary to determine the concentrations of the reactive oxidants in the atmosphere from field studies. Then using these concentrations and the rate constant for the reaction of chemical with the oxidant, it is possible to calculate the environmental rates for the various processes. In the following sections we review the data on the concentrations of OH and ozone.

Determination of OH Concentrations in Polluted Air

In several studies, automobile emissions have been monitored in sufficient detail to allow observation of decay of specific hydrocarbons as a function of time. From these data it is possible to estimate the atmospheric OH concentrations. The most successful such experiment was the Los Angeles Reactive Pollutant Program (LARPP) supported jointly by the Coordinating Research Council and the Environmental Protection Agency. Calvert (1976) was the first to show that in the same air parcel, the more reactive hydrocarbons decreased faster than the less reactive hydrocarbons. The most satisfactory data were obtained by following the ratios of 1-butene/acetylene and propene/acetylene. 1-Butene, propene, and acetylene come almost exclusively from automobiles; acetylene is relatively unreactive and therefore is a good marker for dilution.

In typical examples, during the hours 8:00 AM to 2:00 PM the molar ratio of propene to acetylene decreased from 0.36 to 0.20. Similarly, the ratio of 1-butene to acetylene decreased from 0.9 to 0.2 during the same time. Making the valid assumption that acetylene does not react appreciably, we can estimate the OH radical concentration from these data using the expression

$$\ln\left\{\frac{[RH]}{[S]}\right\}_o - \ln\left\{\frac{[RH]}{[S]}\right\}_t = k_{OH}[OH] \tag{5.52}$$

or

$$[OH] = \left\{\ln\left\{\frac{[RH]}{[S]}\right\}_o - \ln\left\{\frac{[RH]}{[S]}\right\}_t\right\} k_{OH}^{-1} \tag{5.52a}$$

where $\{[RH]/[S]\}_o$ and $\{[RH]/[S]\}_t$ represent the initial and final molar ratios of reactive hydrocarbon to standard (acetylene), and k_{OH} is the rate constant for reaction of OH with the reactive hydrocarbon. Thus from this expression the OH concentration is estimated from the observed change in ratio of [RH]/[S] and the experimental value for k_{OH}.

By following propene and 1-butene and 2-butene plus isobutene combined, Calvert determined values of [OH] that were in reasonable agreement ($\sim$ 7 x

10^5 molec cm^{-3}). Following the change of alkanes, such as n-butane, gives much higher values of OH. It is believed that these values are generally higher because the alkanes have a number of sources, whereas the simple alkenes have only one source; hence, the ratio of alkane to acetylene can be sensitive to mixing of air parcels with varying origins. Because alkanes are much less reactive than alkenes, small changes in the ratios lead to large uncertainties. Statistical analysis of the data based used in estimating the [OH] concentration by Singh et al. (1978), at SRI, indicates that the alkane data base shows considerably more scatter and the estimates of [OH] have poor correlation coefficients and considerably larger uncertainty bounds. Therefore, the OH value of 0.7×10^6 molecules/cc (0.3×10^{-7} ppm) obtained from the alkene data is the best estimate of OH in polluted urban atmosphere using this technique. The evidence for the nonurban atmosphere (downwind from the urban area) places the OH concentration slightly lower but within the limits of experimental uncertainty.

The general technique described above assumes that the air parcel that is being tracked and from which samples are being collected is isolated. Although dilution may occur both the reactive hydrocarbon and standard (acetylene) will be diluted at the same rate and thus their ratio will not be affected. Generally, vertical mixing below the inversion layer occurs quickly between ground level and the base of the inversion layer, but mixing across the inversion layer is slow, so that mixing of air parcels with older air parcels above the inversion layer and where the reactive hydrocarbon to acetylene ratio is low is not expected to occur. However, the sample air parcel is subject to fresh emissions from all sources, including automobiles, that produce the reactive hydrocarbons and acetylene in the initial ratio. This constant addition of these hydrocarbons will tend to make the calculated value of OH lower than its actual value in the cases where fresh emissions enter the air parcel. This problem clearly is most important in the urban areas, and therefore the measured OH value should be considered a lower limit in these cases. However, the effect should not be more than a factor of two. Because emissions in the nonurban areas should be minimal, OH concentration estimates for such areas would be expected to approximate reliably the true value. Thus, the small difference observed between urban and nonurban OH values may only appear so because of the effect of continued emissions in urban studies. If a correction for emission could be made, we might find that estimates of the urban OH concentrations are a factor of two or three larger than those for nonurban areas.

Estimation of Average Tropospheric OH Concentration. Our modern industrial civilization produces and emits a number of compounds that have long lifetimes in the atmosphere and no natural sources. Some of these compounds, especially the Freons, have no known chemical loss mechanisms in the troposphere, although others are subject to slow reactions in the troposphere. By comparing the amount of compound emitted to the atmosphere with what is found, it is possible to determine loss reaction rates. A compound of considerable interest in this regard is methylchloroform (1,1,1-trichloroethane). This compound has been produced for use largely as a nonreactive and nontoxic cleaning solvent, and essentially all that is produced is eventually lost to the atmosphere. The tropospheric chemistry is limited only to reaction with OH

$$CCl_3CH_3 + OH \longrightarrow HOH + CCl_3CH_2\cdot \qquad (5.53)$$

Thus since the quantities of methylchloroform produced must match the material in the atmosphere plus what has reacted with OH and diffused to the stratosphere, careful measurement of the atmospheric concentrations can lead to an estimate of the average OH concentrations according to the equation

$$\frac{d[CH_3CCl\ ]}{dt} = \text{Input Rate} - \frac{1}{\tau}[CH_3CCl_3] \qquad (5.54)$$

$$\frac{1}{\tau} = k_{OH}[OH] + k_D$$

where k_D is the rate constant for diffusion to the stratosphere. Thus, a value of OH can be obtained that is averaged over the total day, all elevations, and all seasons, and it should represent the best value for predicting environmental lifetimes that are sufficiently long that total mixing in the troposphere occurs. Singh (1977; 1977a) has shown that the methylchloroform concentration in the atmosphere is consistent with an atmospheric residence time of about 8 years, which translates to an average tropospheric OH concentration of about 4.1 x 10^5 molec/cc. The concentration is slightly larger in the southern hemisphere than in the northern.

Neely and Plonka (1978) have also analyzed existing methylchloroform data, and based on monitoring data through 1976, they suggest an average tropospheric lifetime of 2 to 4 years. However, atmospheric concentrations projected from their data underpredict more recent monitoring data. Thus a lifetime in this range appears to be too short. Chang and Penner (1978) have recently made a detailed analysis of the methylchloroform problem. Using unpublished monitoring data of Rasmussen, they obtained a lifetime of 11.3 years; random errors of about 10% in the measured atmospheric concentrations could lead to uncertainties in the lifetime of ± 30%. Use of Singh's recent data (1978) would not significantly alter this conclusion. Thus our best estimate of the tropospheric lifetime of methylchloroform is about 11 years, which leads to an average OH radical concentration of about 3 x 10^5 molec/cc, consistent with Singh's original estimate.

Direct Measurement of OH Concentrations. Because of the great importance in accurately knowing how the concentration of OH varies in the atmosphere, considerable effort is being made to measure it using direct methods. Several different techniques have been used.

Perner et al. (1976) have used laser absorption spectroscopy over a 7.8-km path length to measure OH over the city of Julich, Germany. Their results indicate a general upper limit for mid-day concentration of 4 x 10^6 molec/cc, with concentrations as high as 7 x 10^6 molec/cc being observed occasionally.

Wang et al. (1975) have used laser-induced fluorescence to estimate OH in Detroit. Concentration estimates ranged from the detection limit (5 x 10^6 molec/cc) to 6 x 10^7 molec/cc at mid-day. A disadvantage of this technique is the uncertainty as to whether or not the laser light used to induce fluorescence may also be photolyzing other atmospheric components to produce OH and thereby generating spurious concentrations of OH.

Davis et al. (1976) have used laser-induced fluorescence to attempt to measure OH at 7 and 11.5 km. At night they observe less than 2 x 10^6 molec/cc--the detection limit of their experiment. However, in the early afternoon, values of 3.5 to 8.1 x 10^6 molec/cc were observed, with the data possibly showing some dependence on elevation and latitude. However, these data must be considered carefully because of the possibility of the same types of interferences discussed for the Wang et al. experiments.

Further attempts are being made to improve the sensitivity of these various atmospheric measurements. However, at this time most weight should be given to the laser absorption spectroscopy technique because it should be most free from interferences. At present, the best values, based on direct measurements, place the mid-day OH concentration in urban areas at about 4 x 10^6 molec/cc, with lower values being likely to occur more frequently than higher values.

Computational Estimates of Tropospheric OH Concentrations.

Early modeling of the clean troposphere by Levy (1974) indicated ground-level OH concentrations in the range 1 to 6 x 10^6 molec/cc, whereas at the tropopause the values range from 2 to 5 x 10^5 molec/cc. Thus, an overall tropospheric average could be set at about 1 x 10^6 molec/cc. In general, this value was supported by other attempts to model the troposphere. However, recent efforts of Cruzen and Fishman (1977) which make use of the most recent rate constant data, suggest an average northern hemisphere value of 2 to 4 x 10^5 molec/cc. Correcting for a higher southern hemisphere value gives total troposphere average of 4 to 8 x 10^5 molec/cc, about one-half of earlier estimates. At ground level, the estimates indicate a range of 2 to 4 x 10^6 molec/cc at noon.

Computer simulation of the polluted atmospheric chemistry, which was developed to predict ozone, can be used to predict OH concentrations. For simulation of smog chamber data the values depend on reactant concentrations but fall in the range 2 to 10 x 10^6 molec/cc (Hendry et al., 1978). Conditions that most clearly match the urban atmospheric conditions indicate OH concentrations of 2 to 6 x 10^6 molec/cc.

Summary of OH Concentrations Data. Our best picture of how the OH concentration varies in the atmosphere may be summarized as follows.

(1) At ground level at mid-day in the highly polluted troposphere, the OH concentration ranges from 2 to 8 x 10^6 molec/cc, whereas in the clean troposphere the range is 2 to 4 x 10^6. In moderately polluted air the OH concentration may drop to 1 x 10^6 molec/cc or below.

(2) OH concentration decreases with increasing elevation by at least a factor of 10 from ground level to the tropopause.

(3) At ground level the annually averaged concentration is 5 to 10 x 10^5 molec/cc.

(4) The best diurnal, seasonal, and elevation averaged tropospheric concentration is 4 x 10^5 molec/cc. In the northern hemisphere the

best value is 2 to 3 x 10^5 molec/cc, and in the southern hemisphere the value is 4 to 6 x 10^5 molec/cc.

Determination of Ozone Concentrations

Figure 5.5 represents the annual averaged distribution of ozone in the troposphere as a function of latitude and elevation based on ozonesonde data (Fishman and Crutzen, 1978). In general, there is a gradient from higher elevations to lower due largely to ozone mixing into the troposphere from the stratosphere. Ground-level concentrations are between 0.5 to .8 x 10^{12} molec cm^{-3} (20 to 30 ppb). A realistic tropospheric average is 1 x 10^{12} molec cc^{-3} (40 ppb) ozone, with the value being somewhat higher in the northern hemisphere and lower in the southern hemisphere. This difference in value between hemispheres reflects largely a difference in the rate of photochemical production of ozone due to the higher CO concentrations in the northern hemisphere.

In polluted areas, the ground-level concentrations can easily increase to 4 x 10^{12} molec cm^{-3} as a result of photochemical reactions of the higher concentrations of hydrocarbons and nitrogen oxides that are found there (Lonneman et al., 1976). Ozone often continues to develop downwind from large metropolitan areas to give higher than average concentrations (Bufalini, 1977). These high values will have localized effects on ozone chemistry but will generally decrease at night at the surface and have little effect on the average tropospheric ozone concentration.

5.7.5 Design of Laboratory Test Methods

Photochemical Reaction

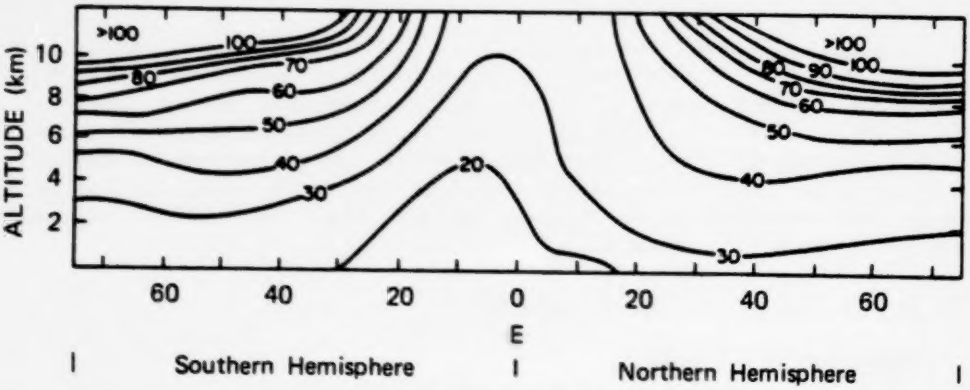
Screening. Section 5.7.2 shows how rates of photochemical reaction may be calculated from the absorption spectrum data, quantum yield, and solar intensity data according to the equation

$$k_p = \phi \Sigma \sigma_\lambda J_\lambda \qquad (5.55)$$

For developing a screening test for photolysis, we recommend that the absorption spectra be obtained and that the integration with solar intensity data be performed assuming unit quantum yields. This assumption is valid for a number of photochemical processes, as shown in Table 5.16. For those cases where the quantum yield is smaller than unity, the estimated value k_p is a reliable upper limit, signified by $\bar{k}_p$,

$$\bar{k}_p = \Sigma \sigma_\lambda J_\lambda \qquad (5.56)$$

Having an upper limit for k_p is still useful because in most cases the estimate will be orders of magnitude less than the rate constants for reaction with OH or O_3 because of the weak absorption of most organic chemicals in the solar spectrum.



Contours in parts per 10^9 by volume

SOURCE: Fishman and Crutzen, 1978.

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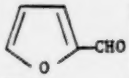
FIGURE 5.5 AVERAGE ANNUAL DISTRIBUTION OF OZONE

Table 5.16

EXAMPLES OF GAS PHASE PHOTOLYSIS PROCESSES, QUANTUM YIELDS, AND ENVIRONMENTAL HALF-LIVES

Compound	Wave-length, nm	Primary Products	Quantum Yield	$t_{1/2}$, days[a]	Reference
CH_2O	303	H• + HCO•	0.760	0.23	b
	313	H• + HCO•	0.735		
	323	H• + HCO•	0.519		
	330	H• + HCO•	0.330		
	303	H_2 + CO	0.24		
	313	H_2 + CO	0.26		
	323	H_2 + CO	0.48		
	330	H_2 + CO	0.67		
CH_3CHO	313	CH_3• + CHO	∿ 0.5	1.1	c
$CH_3C(O)CH_3$	313	$CH_3C(O)$• + CH_3	∿ 1.0	1.8	d
	313-366	uncertain	0.006	0.55	e.f
CF_3NO	540-780	CF_3• + NO	∿ 1.0	0.003	d
CH_3NO_2	313	uncertain	0.6	2.3	g,d
CH_3ONO	366	CH_3O• + NO	0.76	0.014	h
CH_3ONO_2	313	CH_3O• + NO_2	∿ 0.5	40	d
CH_3Br	254	CH_3• + Br	∿ 1.0	1.5×10^3	i
CH_3I	254	CH_3 + I	∿ 1.0	4.4	d
$CH_3N_2CH_3$	366	$2CH_3$ + N_2	1.0	.13	d
H_2O_2	254	2HO•	1.0	2.9	j,d
$(CH_3CH_2)_4Pb$	300-340	uncertain	∿ 1.0	0.30	k

[a] Calculated for June 22 and 30°N from data in table and absorption cross sections over the range 290-800 nm reported by Calvert and Pitts (1966); calculations assume that the reported quantum yields, which were obtained in most cases in the absence of oxygen, apply in the environment.

[b] Horowitz and Calvert (1978).

[c] Weaver, Meagher, and Heicklen (1976/77).

[d] Calvert and Pitts (1966).

[e] Gandini, Parsons, Back (1976).

[f] Gandini, Hackett, Back (1976).

[g] Honda, Mikumi, Takahasi (1972).

[h] Wiebe, Villa, Hellman, Heicklen (1973).

[i] Frank and Hanrahan (1978).

[j] Molina, Schinke, Molina (1977).

[k] Harrison and Laxen (1978).

In determining the absorption spectrum care should be taken in estimating absorption coefficients where the absorbance is small, because even a coefficient of 0.1 cm-M over a broad region of the solar spectrum can be sufficient to account for a relatively rapid rate of photolysis. In general, the use of long-path uv cells increases the accuracy of the absorption coefficient, especially when it is small and the vapor pressure is low. For example, in a 10-cm cell, approximately 20 torr of compound having cross section of 1 x 10^{-22} (0.1 M-cm) will give an absorbance of 0.001. However, in a 10-meter long-path cell, only 20 μm are necessary to obtain the same absorbance. Since many compounds will have both small cross sections and low vapor pressures, the long-path cell is essential for obtaining gas phase absorption spectra. An alternative to using a long-path cell in these cases is to determine the spectra of the chemical dissolved in solvent that does not absorb in the solar region. Acetonitrile, cyclohexane, and 1,4-dioxane are examples of solvents that could be used. In general, solvents such as water, organic acids, and alcohols should be avoided because of their greater ability to perturb absorption spectra. The spectra should be obtained over as wide a range of concentrations as possible in a 10-cm cell, in at least two solvents. Values of k_p or $\bar{k}_p$ based on absorption data obtained from liquid phase spectra should always be labeled as such.

Detailed Tests. For the detailed measurements, the quantum yield is determined by laboratory measurement at a single wavelength and incorporated into the photochemical reaction rate calculation equation 5.40. This allows $\bar{k}_p$, the upper limit for the photochemical reaction, to be converted to a true value of k_p.

$$k_p = \Phi \bar{k}_p \tag{5.47}$$

The quantum yield (ϕ) for a photochemical reaction is the fraction of light absorbed by a molecule that results in chemical reaction

$$\phi = \frac{\text{moles chemical reaction}}{\text{einsteins of light absorbed}} = \frac{\Delta C_c}{I_a^c} \tag{5.58}$$

The value for the moles of chemical reaction is determined by measuring the decrease in concentration (ΔC_c) during the time the compound is exposed to light in the photoreactor. The amount of light absorbed (I_a^c) is calculated from the expression

$$I_a^c = I_o(1 - e^{\sigma_c \ell C_c^{av}})t_c \tag{5.59}$$

where I_o is the intensity of the light photons/s in the photolysis cell and to which the compound is exposed. α_c is the cross section (cm^2 $molec^{-1}$) at the wavelength of the photolytic beam, ℓ is the path length (cm), C_c^{av} is the average concentration (molec cm^{-3}), and t is time (seconds). At value of I_o/I less than 1.02, this expression is approximated by

$$I_a^c = I_o \sigma_c \ell C_c t_c. \qquad (5.59a)$$

I_o is determined by following the decrease under the same conditions of a standard compound (actinometer) for which both the quantum yield, ϕ_s, and cross section, σ_s are known. The I_o may be evaluated from the expression

$$I_o = \Delta C_s / \phi_s (1 - e^{\sigma_s \ell C_s^{av}}) t_s \qquad (5.60)$$

or at $I_o/I < 1.02$

$$I_o = \Delta C_s / \phi_s \sigma_s \ell C_s t_s \qquad (5.60a)$$

where the subscript s signifies constants for the standard compound or actinometer in the calibration experiment.

Combining both equations (5.59) and (5.60) or (5.59a) and (5.60a) gives the following expression:

$$\phi_c = \phi_s \left(\frac{\Delta C_c}{\Delta C_s}\right) \frac{(1 - 10^{\sigma_s \ell C_s^{av}}) t_s}{(1 - 10^{\sigma_c \ell C_c^{av}}) t_c} \qquad (5.61)$$

$$= \phi_s \frac{\Delta C_c}{\Delta C_s} \frac{\sigma_s}{\sigma_c} \frac{C_s}{C_c} \frac{t_s}{t_c} \qquad (5.58)$$

Alternatively, the disappearance of both the compound, C, and actinometer, S, may be expressed as first-order rate constants, k_{pc} and k_{pa}, from the equations

$$\ln[C_c]_o/[C_c]_t = k_{pc} \cdot t_c \text{ and } \ln[C_s]_o/[C_s]_t = k_{pa} \cdot t_a \qquad (5.62)$$

where $k_{pc} = I_o \phi_c \sigma_c \ell$ and $k_{pa} = I_o \phi_s \sigma_s \ell$. In this case, the quantum yield, ϕ_c, may be determined directly from the expression

$$\phi_c = \phi_a (k_{ps}/k_{pc})(\sigma_c/\sigma_s) \qquad (5.63)$$

The techniques for determining quantum yields, the primary measurement in all photochemical studies, have been well developed. Chapter 3 discusses briefly techniques for quantum yield measurements; however, a number of references discuss the techniques in detail (Calvert and Pitts, 1966; deMayo and Shizuka, 1976; Murov, 1973). For gas-phase studies an optical bench arrangement is preferred as opposed to a merry-go-round type of reactor. Figure 5.6 illustrates one possible arrangement. The light is generated by an arc lamp (generally a medium-pressure mercury source). Stray light is reduced by a series of slits (S) and the beam is collimated by a series of lenses (L). The second lens has a long focal length to focus the beam sufficiently to

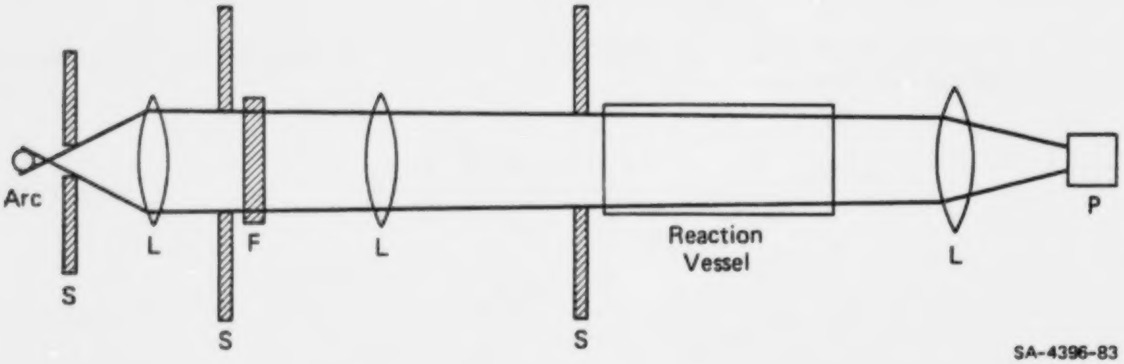

Arc
S
L
S
F
L
S
Reaction Vessel
L
P
SA-4396-83

FIGURE 5.6 PHOTOCHEMICAL APPARATUS FOR DETERMINING QUANTUM YIELDS

minimize light striking the reactor walls. The third lens concentrates the light beam so that a photocell can monitor the intensity. Although the monitoring system (P) is not essential, it does provide information regarding the stability of the lamp that otherwise could be obtained only by additional standard runs. The light is filtered to isolate the simple emission bond from the lamp that best matches absorption by the compound under study. The filters (F) can be either chemical solutions or commercially available glass filters. The effectiveness of any filtering system over the range 190-800 nm should be checked with a uv-visible spectrometer before use. Because the chemical solutions are not stable indefinitely, they should be checked frequently to ensure their stability.

Because the refractive index in glass varies with wavelength, the light beam cannot be properly aligned visually if the wavelength selected for study is less than 400 nm. If the focal length at a visible wavelength is known, it is possible to calculate the focal length at the desired wavelength for the lenses using the literature refractive indexes for the glass at each wavelength. An alternate method of tracing invisible ultraviolet light is to use filter paper impregnated with a fluorescent material such as anthracene.

As a word of caution, it is important the the investigator wear eye protection to prevent eye exposure to either the direct or reflected radiation of ultraviolet light. Similarly, skin should be shielded with clothing to avoid severe sunburn.

Reaction with OH

Screening. In Section 5.7.3 we showed that the rate constant for reaction with OH can be estimated for a wide variety of compounds using equation (5.51) and data in Tables 5.1 to 5.3. This estimation method is used to estimate the OH rate constant at the screening level. In most cases, when properly applied, this technique is expected to be reliable within a factor of two.

Detailed Tests. The method of choice for measuring the rate constant for reaction of a chemical with OH is to generate OH by pulse photolysis of an OH source such as H_2O or H_2O_2 and then to follow the OH decay either by resonance fluorescence or laser-induced fluorescence. The kinetic expression is

$$\frac{d[OH]}{dt} = k[OH][C] \qquad (5.64)$$

or

$$\ln\frac{[OH]_i}{[OH]} = k[C]_t \qquad (5.65)$$

This general technique is discussed fully in the literature (Atkinson et al., 1975).

The proposed procedure using photolysis of a mixture of the chemical, reference compound, and HONO (Niki et al., 1978a; Hoshino et al., 1978) determines the rate of reaction toward OH relative to a standard compound for which the absolute rate constant toward OH is known. In general, the precision of the proposed technique is not as good as that of fluorescence techniques, but it can be applied to a wider range of compounds and requires only methods which are familiar to most chemists.

Reaction with Ozone

Screening. The screening test for reaction of ozone requires no laboratory measurements. Instead, the rate constant for reaction is estimated by comparing the reactive function(s) of the compound with those of other compounds where the ozone rate constant has been measured. Table 5.7 lists the reactivity of various reactive structures based on data from Table 5.14. Saturated structures--such as alkanes, chloro and fluoroalkanes, simple alcohol, organic acids, esters, ketones, and aldehydes--all react very slowly with ozone with $k_{O_3} = < 1\ M^{-1}\ s^{-1}$, which gives environmental half-lives on the order of 100 years. On the other hand, olefinic compounds react rapidly with ozone with rate constants of 1000 to 10,000 $M^{-1}\ s^{-1}$, which corresponds to environmental half-lives of about 1 to 20 days. In these cases it will be possible to estimate the rate constant from the data in Table 5.7.

Detailed Tests. The determination of the rate constants for the reaction of ozone with organic compounds may be obtained by following the change of either reactant with an excess of the other reactant. The rate expressions are

$$d[RH]/dt = k[O_3][RH]$$

$$\ln[RH]_0/[RH] = k[O_3]$$

where $[O_3] \cong$ constant;

$$d[O_3]/dt = k[O_3][RH]$$

$$\ln[O_3]_0/[O_3] = k[RH]$$

where $[RH] \cong$ constant. A variety of techniques have been used to measure the change in reactants (Japar et al., 1974, Herron and Huie, 1974; Bufalini and Altshuller, 1965). The method recommended in Section 5.6.3 has been selected to minimize equipment requirement without significantly reducing accuracy.

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Appendix 5.A

STATISTICAL ANALYSIS FOR k_{OH}^{C}/k_{OH}^{S} *

In the proposed process, the concentrations of two substances, A and C (where C is a standard with known reaction rate k_C), are measured initially and after a lapse of time t. The final concentrations A_t and C_t are assumed to be related as

$$\ln\frac{A_o}{A_t} = \frac{k_A}{k_C}\ln\frac{C_o}{C_t}$$

where A_o and C_o are the initial concentrations, and k_A and k_C are the reaction rates. We assume that the concentration measurements are log normally distributed with variances $\sigma^2(\ln A) = \sigma_A^2$ and $\sigma^2(\ln C) = \sigma_C^2$, neither of which depends on t. The parameter ratio $R = k_A/k_C$ is to be estimated. This could best be done by measuring $y = \ln\frac{A_o}{A_t}$ and $x = \ln\frac{C_o}{C_t}$ for a number of different values for t and carrying out a regression of y on x. However, current practice is to select a suitable value of t and estimate R from y/x for the selected t.

From the assumptions made, y and x are normally distributed with variances $\sigma^2(y) = 2\sigma_A^2$ and $\sigma^2(x) = 2\sigma_C^2$. Let $\bar{y} = E(y)$ and $\bar{x} = E(x)$ be the expected values of y and x, respectively. Assuming that x and y are independent, the transformations $u = (x-\bar{x})/\sigma_x$ and $v = (y-\bar{y})/\sigma_y$ yield normally distributed variables u and v with zero means and unit variances. Their probability densities are $p(u) = \frac{1}{\sqrt{2\pi}}e^{-\frac{1}{2}u^2}$ and $p(v) = \frac{1}{\sqrt{2\pi}}e^{-\frac{1}{2}v^2}$, with a joint probability density of $p(u,v) = \frac{1}{2A}e^{-\frac{1}{2}(u^2+v^2)}$. The ratio R can now be expressed in terms of u and v as

$$R = \frac{\bar{y} + v\sigma_y}{\bar{x} + u\sigma_x}$$

We are interested in E(R) and $\sigma^2(R) = E(R^2) - [E(R)]^2$. We have $E(R) = E(y)E(\frac{1}{x})$ and $\sigma^2(R) = E(y^2)E(\frac{1}{x^2}) - [E(y)E(\frac{1}{x})]^2$ where

$$E(y) = \bar{y} + \sigma_y E(v) = \bar{y}$$

$$E(y^2) = E(\bar{y}^2 + 2\sigma_y\bar{y}v + \sigma_y^2 v^2) = \bar{y}^2 + \sigma_y{}^2$$

since $E(v) = 0$ and $E(v^2) = 1$. However, $E(\frac{1}{x})$ and $E(\frac{1}{x^2})$ are given by

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*This analysis was carried out by Dr. Francis W. Dresch.

$$\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\frac{1}{(\bar{x}+u\sigma_x)^n}e^{-\frac{1}{2}u^2}du = \frac{1}{\sqrt{2\pi}(\bar{x})^n}\int_{\infty}^{\infty}\frac{1}{(1+\frac{\sigma_x}{\bar{x}}u)^n}\,e^{-\frac{1}{2}u^2}du$$

for n = 1 and 2. Singularities enter when $u = -\frac{\bar{x}}{\sigma_x}$. To avoid these, the assumed normal distribution $p(u) = \frac{1}{\sqrt{2\pi}}e^{-\frac{1}{2}u^2}$ can be replaced by a truncated normal distribution

$$p(u) = \begin{cases} \frac{1}{\sqrt{2\pi}}e^{-\frac{1}{2}u^2} / \frac{1}{\sqrt{2\pi}}\int_{-L}^{L}e^{-\frac{1}{2}u^2}du & \text{if } -L < u < L \\ 0, \text{ otherwise} & \end{cases}$$

$$E(u^n) = \frac{1}{a}\int_{-L}^{L}u^n e^{-\frac{1}{2}u^2}du,$$

where $a = \int_{-L}^{L} e^{-\frac{1}{2}u^2}du = E(u^0)$

$$E(u^n) = \frac{1}{a}\{[-u^{n-1}e^{-\frac{1}{2}u^2}]_{-L}^{L} + (n-1)\int_{-L}^{L}u^{n-2}e^{-\frac{1}{2}u^2}du\}$$

$$= (n-1)E(u^{n-2}) - b_{n-1}L^{n-1}$$

where $b_{n-1} = \frac{2}{a}e^{-\frac{1}{2}L^2}$ if n-1 is odd and 0 otherwise. We have

$$E(u^0) = 1$$

$$E(u) = 0$$

by direct evaluation of $\frac{1}{a}\int_{-L}^{L}e^{-\frac{1}{2}u^2}du = \frac{a}{a} = 1$ and $\frac{1}{a}\int_{-L}^{L}ue^{-\frac{1}{2}u^2}du = \frac{1}{a}[-e^{-\frac{1}{2}u^2}]_{-L}^{L} = 0$. From the recursion formula

$$E(u^2) = E(u^0) - b_1L = 1 - b_1L,$$

where $b_1 = 2e^{-\frac{1}{2}L^2}/\int_{-L}^{L}e^{-\frac{1}{2}u^2}du$

$$E(u^3) = E(u) - b_2L^2 = 0,$$

since $E(u) = 0 = b_2$. All expectations of odd powers of u vanish, as can be seen either from the recursion process or from symmetry

$$E(\frac{1}{\bar{x}}) = \frac{1}{a\bar{x}}\int_{-L}^{L}(1 + u\frac{\sigma_x}{\bar{x}})^{-1}$$

and

$$E(\frac{1}{x^2}) = \frac{1}{a\bar{x}^2}\int_{-L}^{L}(1 + \frac{\sigma_x}{\bar{x}}u)^{-2}e^{-\frac{1}{2}u^2}du$$

Expanding $(1 + \frac{\sigma_x}{\bar{x}}u)^{-n}$ as binomial series for n = 1 or 2 gives

$$E(\frac{1}{x}) = \frac{1}{\bar{x}}E\{1 - \frac{\sigma_x}{\bar{x}}u + (\frac{\sigma_x}{\bar{x}})^2u^2 - (\frac{\sigma_x}{\bar{x}})^3u^3 \ldots \}$$

$$= \frac{1}{\bar{x}}\{1 + (\frac{\sigma_x}{\bar{x}})^2(1 - b_1L) + (\frac{\sigma_x}{\bar{x}})^4E(u^4) +..\}$$

$$E(\frac{1}{x^2}) = \frac{1}{\bar{x}^2}E\{1 - 2\frac{\sigma_x}{\bar{x}}u + 3(\frac{\sigma_x}{\bar{x}})^2u^2 - 4(\frac{\sigma_x}{\bar{x}})^3u^3 +.. \}$$

$$= \frac{1}{\bar{x}^2}\{1 + 3(\frac{\sigma_x}{\bar{x}})^2(1 - b_1L) + 5(\frac{\sigma_x}{\bar{x}})^4E(u^4) +... \}$$

$$E(R) = E(y)E(\frac{1}{x}) = \bar{y}\cdot\frac{1}{\bar{x}}\{1 + (\frac{\sigma_x}{\bar{x}})^2(1 - b_1L) +.. \}$$

$$E(R^2) = E(y^2)E(\frac{1}{x^2}) = \frac{\bar{y}^2 + \sigma_y^2}{\bar{x}^2}\{1 + 3(\frac{\sigma_x}{\bar{x}})^2(1 - b_1L) +.. \}$$

$$[E(R)]^2 = (\frac{\bar{y}}{\bar{x}})^2\{1 + 2(\frac{\sigma_x}{\bar{x}})^2(1 - b_1L) + .. \}$$

and

$$\sigma^2(R) = \frac{\sigma_y^2}{\bar{x}^2}\{1 + 3(\frac{\sigma_x}{\bar{x}})^2(1 - b_1L) +.. \} + (\frac{\bar{y}}{\bar{x}})^2\{(\frac{\sigma_x}{\bar{x}})^2(1 - b_1L) +..\}$$

$$= (\frac{\bar{y}}{\bar{x}})^2\{\frac{\sigma_y^2}{\bar{y}^2}[1 + 3(\frac{\sigma_x}{\bar{x}})^2(1 - b_1L) +..] + [(\frac{\sigma_x}{\bar{x}})^2(1 - b_1L) +..]\}$$

$$\frac{\sigma^2(R)}{[E(R)]^2} = \{\frac{\sigma_y^2}{\bar{y}^2} + (\frac{\sigma_x}{\bar{x}})^2(1 - b_1L) +...\} \div \{1 + 2(\frac{\sigma_x}{\bar{x}})^2(1 - b_1L) +.. \}$$

For $L = 3$, $b_1 = 0.00675$ and $1 - b_1L = 0.979$. For $L = 5$, $b_1 = 3\cdot10^{-6}$ and $1 - b_1L = 0.999985$. Thus if $5\frac{\sigma_x}{\bar{x}} < 1$ or $\bar{x} > 5\sigma_x = 5\sqrt{2}\sigma_c \cong 7\sigma_c$ and if second and higher terms in $\frac{\sigma^2(x)}{\bar{x}^2}$ and $\bar{x}\ \frac{\sigma^2(y)}{y^2}$ are neglected[*]

$$\frac{\sigma^2(R)}{[E(R)]^2} \cong \frac{\sigma^2(y)}{\bar{y}^2} + \frac{\sigma^2(x)}{\bar{x}^2}$$

Note that

$$E(R) \cong \frac{\bar{y}}{\bar{x}}[1 + (\frac{\sigma_x}{\bar{x}})^2(1 - b_1L)].$$

Thus, $\frac{y}{x}$ as an estimate of $\frac{\bar{y}}{\bar{x}}$ is about 4% high if $\bar{x} > 5\sigma_x$ or $5\sqrt{2}\sigma_c$.

---

[*] This includes terms such as $\frac{\sigma^4(x)}{\bar{x}^4}$, $\frac{\sigma^4(y)}{\bar{y}^4}$, and $\frac{\sigma^2(x)\sigma^2(y)}{\bar{x}^2\bar{y}^2}$.

CHAPTER 6. AQUATIC BIODEGRADATION

by

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6. AQUATIC BIODEGRADATION

6.1 INTRODUCTION

Biodegradation is one of the most important processes for transformation of chemical compounds when they enter into natural environments. Many organic chemicals are used by living cells for carbon and energy sources. Microorganisms metabolize a wide variety of organic compounds, including man-made xenobiotic chemicals, and play major roles in biodegradation. It is important to determine biodegradation rate constants for quantitative comparison with other, different pathways. This section evaluates methods available for obtaining the data needed to calculate rates of primary biodegradation in aquatic systems. From these methods we have selected a few to use as screening test protocols for biodegradation. No recommendation is made as to selection of test protocols for detailed study; however, principles of rate constant determination are discussed in the section on kinetics.

6.2 SUMMARY

Screening test protocols for biodegradation of chemicals in water have been tentatively prepared to enable investigators to obtain preliminary information about primary biodegradation of chemicals. The river die-away method (RDA) provides acclimation times and half-lives after the initiation of biodegradation. The semicontinuous activated sludge method (SCAS) provides data on the percent biodegraded in 24 hours of fill-draw cycle. These two test protocols are widely used, simple, and cost-effective, representing the best state of the art among many methods developed. However, these procedures have limited value in estimating the fate of toxic substances in the environment. A protocol of detailed testing for biodegradation rates was not presented because of the complexities of biodegradation. Relatively few investigations have been conducted to correlate biodegradation and biomass. Kinetic descriptions which have been developed and available methods are discussed in the text.

Many factors affecting biodegradation are discussed and aquatic biodegradation test methods are reviewed.

6.3 CONCLUSIONS

The RDA and SCAS methods are recommended as screening tests for biodegradation protocol as the best test procedures currently available. The procedures have some limitations for use as completely acceptable aquatic biodegradation test protocols for all chemicals. Methods for obtaining the data necessary to calculate rate constants and half-lives for biodegradations are described, although no detailed test protocol is proposed. Further research is needed in this area.

6.4 RECOMMENDATIONS

The screening test methods should be evaluated in the laboratory for applicability to several chemicals of environmental concern, which could then be used as reference standards in testing other chemicals. The reference chemicals should include representatives of a wide range of chemical groups. The water samples should be collected from different places and at different times, with selected chemicals being used for testing reproducibility of the results. Research is needed to develop test procedures for detailed rate constant studies.

6.5 SCREENING TEST

6.5.1 Purpose

The screening test protocols are intended to provide preliminary information on primary biodegradation or persistence of chemicals in aquatic environments.

6.5.2 Protocols

Many methods have been developed for testing biodegradability of chemicals in aquatic systems (Howard et al., 1975). These methods differ significantly in approach and in complexity of operation. The numerous complicated environmental factors and the inherent lack of precision in biological systems make the study of biodegradation complex.

Chemicals may be degraded in aquatic environments, such as rivers, ponds, or lakes, with relatively low microbial populations; or in sewage or waste biological treatment plants or in polluted waters with relatively high microbial populations. River die-away tests and semicontinuous activated sludge methods are representative of two different types of tests. These two methods are recommended in this protocol for screening tests. However, these methods have limited uses as a completely acceptable standard procedure for testing biodegradability of all organic chemicals. Selection and modification of a biodegradation test for a particular chemical should take into account the chemical's major route of entry into the natural environment as well as physical, chemical, and toxicological properties of the chemical. The procedures described below are for testing relatively water soluble nonvolatile chemicals of low toxicity.

For each set of tests, extra test vessels containing chemicals known to be biodegradable should be included as reference standards for evaluating the biodegradation capabilities of the water samples.

River Die-away Test (RDA)

Of all the tests, the RDA is the most simple and the closest to natural environmental conditions. The test consists of adding test chemicals to natural water samples; degradation is followed as a function of time. There is variability in chemical compositions and microbial populations in natural waters, and these may cause variation in the test results. However this method will provide preliminary information about the acclimation periods and degradation rates. It will also provide acclimated mixed culture degradation systems for enrichment processes that can be used for detailed studies.

The RDA test is as follows. Water and sediment (of about 5 percent of the volume of water) are obtained from a river that is large enough to have only slight variability in quality and flow. The water and sediment are mixed thoroughly and the sediment is allowed to settle. The supernatant is syphoned off and filtered through a layer of glass wool or cloth to remove large floating particles. Then 2 liters of the water sample is dispensed in a 4-liter glass container (or 1 to 5 liters in a 2- to 9-liter vessel).

Concentrations of chemical depend on solubilities, realistic environmental contamination levels, and sensitivities of analytical methods. Concentractions in the neighborhood of 1 $\mu g/ml^{-1}$ are recommended. Each chemical is added in duplicate to water samples as aquatic stock solution. If the chemical is low aqueous solubility compound, it may be added with a minimum amount of solubilizing solvent, such as dimethyl sulfoxide, which is highly resistant to microbial degradation but not toxic to microbes. Sterile water samples with the test chemical added are used as controls for possible chemical degradation and volatilization. Other chemicals known to be biodegradable may be added to water in other vessels and included in the test run as reference standards monitoring their biodegradation to evaluate the biodegradation capability of the water sample. Extra water samples containing the test chemical plus an analog compound known to be biodegradable, and a possible pollutant present in the environment with the test chemical, may be set up if cometabolic biodegradation is suspected.

At the start, the water sample containers should be agitated or shaken to saturate the water with oxygen. The container is covered with a cotton plug or loose lid to prevent excess evaporation. The water is incubated in the dark at 25°C for up to 8 weeks. The water should be agitated before each sampling for mixing and aeration.

An aliquot of the sample is withdrawn daily or on some other schedule appropriate to the rate of degradation for the test chemical. The sample is extracted with a proper organic solvent for chemical analysis to determine the disappearance of the chemical. If the chemical has a specific visible or ultraviolet (uv) absorption peak, spectrophotometric methods are used for a quick check of the degradation so that the microorganisms may be transferred for culture enrichment. If necessary, a more frequent sampling schedule is set up for monitoring the degradation.

The experiment is completed when the parent chemical has > 90% disappeared or when there has been no change in concentration for more than three days after a period of biotransformation. From the chemical analysis, the acclimation period and rate of degradation can be obtained if sampling is sufficiently frequent to show changes in concentration of the chemical. Microbial plate counts at the time of degradation may be made and used to estimate degradation rate constants, although only a fraction of the microbial population may be responsible for the biodegradation. When degradation is 50 to 80% complete, the microorganisms are transferred into a shaker flask for development of the enrichment culture to be used in detailed studies or for confirmation of the biodegradation.

Semicontinuous Activated Sludge (SCAS)

The semicontinuous sludge test is a modified confirmatory test of the Soap and Detergent Association (1965). The 24-hour cycle of fill-and-draw closely represents the biodegradation in sewage treatment plants or continuously polluted, high-microbial-population environments. The operation is more simple and less costly than the continuous method.

Aeration chambers consist of glass vessels (3-4 liters) with cone-shaped lower parts, fitted with a gas diffuser at the inside bottom of the conical end. The medium is aerated and mixed by passing glass wool filtered sterile air through a glass diffuser into the medium. The aeration period averages 23 hours per day. The aeration rate is maintained at 500 ml/minute; temperature is maintained at 25° ± 3°C.

Activated sludge samples for inoculum are collected from a sewage plant that principally treates domestic wastes. Concentration of the suspended solids is adjusted to approximately 2500 μg/ml with tap water; 1500 ml of this activated sludge is placed into each chamber and the fill-and-draw routine (described later) is begun.

Synthetic sewage stock solution is prepared by dissolving 30.0 g of glucose, 20.0 g of nutrient broth, 13.0 g of K_2HPO_4, 2.5 g of $(NH_4)_2SO_4$ in tap water to make up to 1 liter.

The following incremental chemical feed schedule is used with synthetic sewage to acclimate the organisms:

On Day 0	Feed 2 mg/liter
On Day 1	Feed 4 mg/liter
On Day 2	Feed 6 mg/liter
On Day 3	Feed 8 mg/liter
On Day 4 (finish)	Feed 10 mg/liter

With each run, at least one unit fed a reference standard chemical is included as a control on sludge suitability and operation conditions.

The daily routine is as follows. An aliquot of well-mixed sample is withdrawn for solvent extraction and subsequent analysis (effluent). Aeration is stopped for 30 minutes to allow the material to settle; the upper 1000 ml supernatant is then removed. Aeration is resumed and 10 ml of synthetic sewage stock solution (with enough tap water to make up to 1500 ml) and 10 mg/liter of the test chemical are added. The pH is maintained at 6.5-8.0 with NaOH or HCl, and dissolved oxygen (at least 2 mg/liter) is maintained by the appropriate aeration.

Three days after the addition of chemical has reached the 10-mg/liter level (Day 7), analysis of the chemical is begun. Synthetic sewage stock solution (1 ml) plus the test compound, with the addition of distilled water to 150 ml, make up the influent solution sample for analysis. Both the influent solution sample and the effluent are extracted with organic solvent and analyzed for the test chemical.

Beginning on the fourth day on which chemical feed is 10 mg/liter the percentage of chemical degraded is calculated as follows:

$$\% \text{ degraded (day X)} = \frac{S_i - S_e}{S_i} \times 100$$

S_i = influent analysis and S_i = effluent analysis.

The daily acclimation program is continued until the percentage of chemical degraded is constant (± 10%) for three consecutive days or until the 30th day of the acclimation period. The supernatant may be analyzed to calculate percent removal due to biotransformation and biosorption. Chemical degradation and/or volatilization may be checked by aerating 10 ppm aqueous solution in the chamber at a 24-hour cycle and analyzing it for loss.

This acclimated activated sludge can be used for detailed rate constant studies by centrifuging the sludge and testing it with basal medium/test chemical; or it can be transferred into flasks for enrichment.

6.5.3. Criteria for Screening Test

In the RDA test, if there is no loss of the chemical in sterile water samples, any loss in the nonsterile water samples is assumed to be due to biodegradation. Any loss in the sterile water sample may indicate chemical transformation, volatilization, or adsorption by vessel walls. If the reference standard chemical known to be biodegradable is not degraded, the result is questionable and the test should be repeated with a new water sample. The plot of chemical concentration against time will show acclimation time, biodegradation rate, and extent of parent compound consumption. When biodegradation is apparent, a detailed study is needed to obtain biodegradation rate constants with regard to biomass. The biodegradation can be validated by redosing the water sample with the test chemical or inoculating the acclimated microbes into fresh water containing the chemical. In either case, the chemical will be degraded after a much shorter lag period.

When the test chemical concentration is very low and microbial populations responsible for biodegradation are high, the cell increase due to consumption of chemical is negligible. Under these conditions, a loss of chemical may follow a pseudo first-order transformation, and the half-life can be easily obtained from the curve of chemical concentration versus time on semilogarithmic paper. The half-life is counted from the initiation of biodegradation and does not include acclimation time.

The pseudo-first order rate constant k_b' can be obtained from the slope or half-life ($t_{\frac{1}{2}}$):

$$k_b' = \frac{\ln 2}{t_{\frac{1}{2}}} = \frac{0.693}{t_{\frac{1}{2}}}$$

When cell plate counts were made at the time of degradation, the second-order rate constant k_{b2} in terms of total cell count X can be obtained from k_b':

$$k_{b2} = k_b'/X$$

Thus, the biodegradation rate is:

$$-\frac{dS}{dt} = K_b'S = K_{b2}XS$$

where S is chemical concentration and t is time of degradation.

When cell populations are low and the level of test chemical added can provide substantial cell growth, degradation will be a second order reaction, depending on increasing biomass and decreasing chemical concentration. Under these conditions, after the initiation of biodegradation, second half-life will be shorter than first half-life.

In the SCAS test, biodegradation is expressed as the percent biodegraded in a 24-hour cycle. The chemical with a high percent degradation value, greater than 90 percent, is likely to be biodegraded easily in a sewage treatment plant or a natural environment, and the chemical with the low percentage degradation value is expected to be slowly biodegradable in natural waters. A set of standard chemicals, representative of different groups, should be tested in the future and used as reference and to categorize the biodegradability of test chemicals. When a chemical in the supernatant is analyzed, the percentage removal is the combined result of biodegradation and adsorption by activated sludge.

6.5.4. Rationale

The screening tests recommended above are relatively simple, cost-effective procedures for evaluating biodegradability of organic compounds in two representative aquatic environments. The RDA method most closely simulates natural surface waters and requires the simplest equipment; in addition, the river water samples can be used as sources of microorganisms and nutrients. The data obtained will provide information about acclimation time, rate of biodegradation, and the amount of parent chemical biodegraded. The SCAS method simulates wastewater treatment operations and is simpler and less laborious than other dynamic methods. The data obtained provide information about percent biodegraded in 24-hour cycle operations.

6.5.5. Scope and Limitations

Two screening test protocols for biodegradation are recommended for two different types of aerobic biodegradation: the RDA test simulating biodegradation in natural surface water, and the SCAS test simulating biodegradation in activated sludge systems. The tests are designed to investigate biodegradability of chemicals performed by microorganisms present in water samples at designated temperature and concentration of the test chemical. The procedures are applicable to chemicals that are relatively water-soluble, low volatility, and nontoxic at the level of testing concentrations. Because biodegradation depends on activities of organisms, and microbial populations vary with the site and time at which the water samples are collected, reproducibility of the test results may not be as good as in chemical transformation tests.

There are many other methods for testing biodegradability of chemicals. Because of the many factors affecting biodegradation and natural environments have many variable factors, each method has its limitations. The choice and modification of test methods should consider physical and chemical properties of chemicals as well as the usage and disposal of the chemicals.

The test procedures measure primary biodegradation involving disappearance of the parent chemicals. Because of the nature of biodegradation, to understand how extensively the chemical is mineralized the study of ultimate biodegradability is also important. For this purpose, a method of testing CO_2 evolution, such as that of Gledhill (1975), may be used. The test procedures for anaerobic biodegradation, generally slower than the aerobic process, is not included in these protocols, but this procedure is important for compounds such as some chlorinated hydrocarbons.

6.6 DETAILED TESTS

6.6.1 Purpose

The objective of the test protocol is to provide a uniform procedure for measurement of biodegradation rates and estimation of rate constants under conditions that will enable the investigator to estimate a biodegradation rate at any biomass level at a low concentration of chemical.

6.6.2. Procedures

Relatively few investigations have been conducted to study biodegradation rates in terms of biomass. Not enough information is available to prepare an acceptable protocol at this time, and future studies are needed. In this section we will discuss the available test procedures that can be used to obtain biodegradation rate constants.

Detailed biodegradation rate studies are conducted with acclimated microorganisms. When biodegradation is apparent in screening tests, aliquots of test water containing acclimated organisms may be transferred into shaker flasks containing basal salts medium and test chemical. After several transfers, these mixed populations of enriched culture systems may be used for the rate study. If the biodegradation involves cometabolism, a cometabolic substrate may be added to the medium; the possibility of eventually growing in medium without cometabolic substrate may be studied by decreasing the amount of cometabolic substrate during successive transfers of microbes. The sludge from an SCAS test may be used directly for a rate study.

The biodegradation rate is the function of microbial biomass and chemical concentration. When microorganisms utilize chemical substrates as sources of carbon and energy, there is an increase in biomass. When low concentrations of chemicals are introduced into waters with relatively high concentrations of cells, the microorganisms grown from consumption of test chemical will not significantly affect the total population. However, when microorganism populations are low and chemical concentrations are high enough to alter those populations, the degradation will be a function of cell growth. Specific microbial growth and specific rates of chemical utilization are not linear relative to the chemical concentrations, as discussed in Section 6.7.2.

Several procedures for measuring kinetics have been used with mixed culture systems in which the chemical serves as the sole carbon source:

- Batch degradation with low-level inoculum of microorganisms and with several levels of chemical concentration.
- Continuous culture system biodegradation with several different feeding rates.
- Batch degradation with large microbial populations and low substrate levels.

Principles of these methods are discussed in the kinetics section (6.7.2). Of the three methods, batch degradation with large microbial populations and low substrate levels is the most simple, cost-time-saving procedure.

6.7 BACKGROUND

6.7.1 Definition and Nature of Biodegradation

Biodegradation is a transformation of chemical compounds by the action of organisms. Microorganisms play a key role in the biodegradation of chemicals in aqueous and terrestrial environments because of their abundance in nature, the numbers and types present, their metabolic diversity, large surface-to-volume ratios, rapid multiplication, high rate of mutation, and adaptability of many organisms to grow under a wide variety of environmental conditions. Organisms require an energy source, carbon, and other elements from their environments for their growth and maintenance. In the process they transform many chemicals introduced into the environment. The uniqueness of biodegradation of organic compounds is that, on many occasions, chemical compounds are metabolized by cooperation of a group of microorganisms to mineralized end products--in contrast to other nonbiological processes that usually result in only slight alteration of parent compounds. Metabolic reactions are rapidly catalyzed by enzymes at ambient temperatures at which many nonbiological reactions either will not occur or will do so at slow rates.

Biodegradation can be divided into the following categories (WPCF, 1967):

- Primary biodegradation - biodegradation to the minimum extent necessary to change the identity of the compound.
- Ultimate biodegradation - biodegradation to a) water, b) carbon dioxide and inorganic compounds.
- Acceptable biodegradation - biodegradation to the minimum extent necessary to remove some undesirable property of the compound, such as foaminess or toxicity.

Acceptable biodegradation is the practical goal of environmental biodegradation. To determine that the chemical is environmentally safe, studies of metabolites produced and their toxicity or undesirable charactistics are needed. The definition of undesirable properties may not be clear and may be changed from time to time. Primary biodegradation is the disappearance of parent compounds, and no ultimate conversion of metabolites is considered. In the assessment of biodegradation, the kinetic data obtained are the relations between biomass in the environment and the disappearance of chemicals when introduced. However, the metabolites produced and their eventual transformation need to be understood to accurately assess the overall environmental fate of chemicals.

6.7.2 Kinetics

When an organic chemical is utilized by microorganisms as a sole carbon source and its concentration limits the rate of microbial growth, the widely used Monod kinetic equation (Monod, 1949) can be used to describe the relation between substrate concentration and rate of cell growth in a well-mixed system:

$$\mu = \frac{\frac{dx}{dt}}{X} = \frac{\mu_m S}{K_s + S} \tag{6.1}$$

where X is the biomass per unit volume, μ is the specific growth rate, μ_m is the maximum specific growth rate, S is the concentration of growth limiting substrate, and K_s is the concentration of substrate supporting half maximum specific growth rate (0.5 μ_m).

The rate of substrate utilization is then:

$$- \frac{dS}{dt} = \frac{\mu X}{Y} = \frac{\mu_m}{Y} \bullet \frac{SX}{K_s+S} = k_b \frac{SX}{K_s+S} \tag{6.2}$$

where Y is the cell yield, k_b is substrate utilization constant and equal to μ_m/Y. The constants μ_m, K_s, and Y are dependent on the characteristics of the microbes, pH, temperature, other nutrients, and some other environmental conditions, and are based on the rate of utilization of a growth rate-limiting single substrate by pure microbial cultures. These kinetic expressions can be used to obtain rate constants with mixed culture systems (Paris et al., 1975; Smith et al., 1977). It is possible to choose culture conditions that allow simplification of the Monod expression by making one of its variables constant or one of its constants insignificant. The results of the simplification allow a straightforward estimation of the remaining constants.

When substrate concentration is high and $S \gg K_s$, then equation (6.2) is reduced to:

$$- \frac{dS}{dt} = \frac{\mu_m}{Y} X = k_b X. \tag{6.3}$$

The degradation rate is first order with cell concentration and zero order with substrate concentration.

For many pollutants in the environment, substrate concentrations are very low and $S \ll K_s$; then (6.2) is reduced to:

$$- \frac{dS}{dt} = k_b \frac{XS}{K_s} = k_{b2} XS \tag{6.4}$$

where K_{b2} is a second-order constant

$$k_{b2} = \frac{\mu_m}{YK_s} = \frac{k_b}{K_s} \tag{6.5}$$

The degradation rate is first order with both cell concentrations and substrate concentrations.

Several procedures have been used for measuring kinetics parameters in which the chemical served as the sole carbon source:

- Batch degradation with low-level inocula of washed biodegrading cells.
- Continuous culture degradation.
- Batch degradation with large microbial populations and low substrate levels.

In batch degradation with low levels of inocula, the initial conditions are chosen so that X_o, the original inoculum, is much smaller than the total microbial growth that could be supported by the chemical substrate. During most of the bacterial growth phase, the substrate concentration is practically constant at S_o, the initial substrate concentration. When organisms start to grow after a lag phase of growth, the cell concentration is plotted against time on semilogarithmic paper, and the specific growth rate μ for particular initial chemical concentrations (S_o) can be calculated from the slope. These tests are conducted with different S_o values, and μ is determined for each value of S_o. Then μ_m and K_s can be calculated by the method of Lineweaver and Burk (1934) as it is used in enzyme kinetics. Inverting equation (6.1) and multiplying by S_o results in the following equation:

$$\frac{S_o}{\mu} = \frac{K_s}{\mu_m} + \frac{S_o}{\mu_m} . \tag{6.6}$$

When S_o/μ is plotted versus S_o, the slope of the line is $1/\mu_m$, and the intercept on the S_o axis is $-K_s$. k_b and k_{b2} can be calculated from μ_m, K_s, and cell yield Y, using (6.5).

The method described above is based on measurement of the specific growth rate of microorganisms, and actual consumption of substrate is not considered. In some biodegradations, initial growth rate may not result from assimilation of the test chemical due to, for instance, diauxic utilization of contaminated substrate (e.g., methyl parathion, Smith et al., 1978). In these cases, other kinetic analyses may be used. When cell yield is constant,

$$X = X_o + Y(S_o - S) = X_o + Y\Delta S \tag{6.7}$$

where ΔS is the substrate consumed and Y is $\Delta X/\Delta S$. Then the integration of combined equations (6.2) and (6.7) provides:

$$-\left[\frac{K_s}{X_o+YS_o}+\frac{1}{Y}\right]\ln(X_o+Y\Delta S)+\frac{1}{Y}\ln X_o+\frac{K_s}{X_o+YS_o}\ln\frac{SX_o}{S_o} \qquad (6.8)$$

$$= -\frac{\mu_m}{Y}t = -k_b t$$

where t is the time after initiation of biotransformation, X_o is the biomass of active organisms at the time of initiation, and S_o is the initial substrate concentration. Stratton and McCarty (1967) and Knowles et al. (1965) used these equations to obtain K_s and k_b.

When $X_o \ll YS_o$ and $S_o \gg K_s$, equation (6.8) is reduced to

$$\ln\Delta S = \mu_m t + \ln(\frac{X_o}{Y}). \qquad (6.9)$$

A plot of $\ln\Delta S$ versus t should be a straight line with a slope μ_m.

By modification of (6.8) Moe (1970) obtained:

$$k_b = \frac{-1}{t_2-t_1}\left\{-\left[\frac{K_s}{X_1+YS_1}+\frac{1}{Y}\right]\ln X_2+\frac{K_s}{X_1+YS_1}\ln\frac{S_2X_1}{S_1}+\frac{1}{Y}\ln X_1\right\} \qquad (6.10)$$

where X_1, X_2, and S_1, S_2 are cells and substrate concentrations at times t_1, t_2, respectively. K_s and k_b values can be obtained from experiments with various S_o levels in which X_1, X_2 and S_1, S_2 are measured at t_1, t_2.

In continuous culture degradation systems, once steady-state is established, dilution rate or (residence time)$^{-1}$ at steady-state is equivalent to μ at the concentrations of chemical present in the chemostats or in the overflow from the chemostats. If the dilution rates are changed and new steady-state concentrations are established, new values of μ and S are obtained. The values of K_s and μ_m are calculated by the Lineweaver-Burk plot procedure.

Both batch degradation with low microbial populations and continuous culture methods are labor intensive. In a mixed-culture system, the relative components in the culture mixtures will change during the course of the experiment. In Monod kinetics, cell yield Y is constant. However, due to the production of the intermediate metabolites, which may not be assimilated immediately during the growth, measurement of substrate disappearance does not necessarily correspond to cell synthesis (Mateles and Chain, 1969). This phenomenon is of particular concern at high dilution rates in continuous culture when a significant portion of the metabolite may be washed out, resulting in low cell yield. Errors in kinetic constants may also develop from parasitism or growth of organisms on autolysis products of dying, or dead, organisms.

In batch degradations with large microbial populations and low substrate levels, experiments can be performed in a relatively short time. In these degradations, microbial populations would not change significantly if all of the substrates were utilized for growth purposes. Degradation rates under these conditions are pseudo-first order and can be described by the equation

$$-\frac{dS}{dt} = k_b' S \qquad (6.11)$$

where k_b' is a pseudo-first-order rate constant. A choice of different X_o would give a different value of k_b'. Therefore,

$$k_b'/X_o = k_{b2} \text{ and } -\frac{dS}{dt} = k_{b2} X_o S. \qquad (6.12)$$

k_{b2} is the second-order rate constant for biodegradation. The degradation rate can be calculated when X_o and S are given. The half-life will be:

$$t_{1/2} = \frac{\ln 2}{k_{b2} X_o}$$

Batch degradation with large microbial populations requires the least time, needs no significant changes in total number or relative components of organisms, and is mathematically simple to calculate. k_{b2} can be used to estimate the persistence of a biodegradable chemical in an acclimated environment where the level of pollution is low.

6.7.3 Factors Affecting Biodegradation

Biodegradation involves enzymatic conversion of chemical compounds. The environmental conditions that influence cell growth, enzyme production, and enzyme function will affect biodegradation rates. There are numerous factors that affect biodegradation and their influences are interwoven. Some of the important factors are:

- Physical and chemical properties of chemicals, such as solubility volatility, adsorption, and chemical structure.
- Species, populations, and physiological states of the microorganisms.
- Environmental conditions, such as temperature, pH, and light.
- Chemical components of water, such as dissolved oxygen and inorganic and organic compounds.

Microorganism Source

The microbial communities in natural environments differ significantly in species and numbers present. They not only differ from place to place, but also from time to time at the same place. No single microorganism species possesses all of the enzymes to catabolize all the natural and synthetic compounds, and no environment contains all species. Since biodegradation is performed by the action of organisms, diversity of the microbial community in the environment is one of the most important factors affecting the biodegradability.

In natural environments, microorganisms are always present as complex mixed-population communities that interact with each other. Test compounds may be competitively utilized by several different species, and the metabolites may be utilized by other species and thus be removed from the environment when a single species may not be able to accomplish this. Fast removal of intermediates may either reduce the toxic effects or modify the chemical equilibrium and increase the degradation rate of the parent compound. In the microbial communities, not only do the microorganisms responsible for biodegradation of test chemicals interact with each other, but other groups of organisms also interact with degradation microbes. The interactions between microorganisms are neutralism, commensalism, mutualism, competition, amensalism, parasitism, predation, and antibiosis (Bungay and Bungay, 1968; Fredickson, 1977).

Microorganisms used for testing biodegradations in aquatic environments are generally obtained from river, pond, lake, lagoon, activated sludge, and raw sewage. Activated sludge normally contains a wide variety and a high population of microorganisms and is considered to be a good microbial source for biodegradation studies. River waters have relatively low populations of microorganisms, but a greater variation of species. If it is expected that the chemicals will mainly pollute rivers and lakes, then a river die-away test with natural water will be a better choice.

Many synthetic chemicals to be evaluated are uncommon substrates for microorganisms, and synthesis of enzymes capable of transforming these compounds has to be induced or derepressed. Frequently there are lag periods between the exposure of the chemicals to the organisms and the initiation of biodegradation. A lag--or acclimation--period is required for the organisms to manufacture the enzymes capable of degrading the chemical or for mutant organisms to develop that can degrade the chemicals. A lag period may also result from too small numbers of degradation microbes being initially present in the system. In the early growth state, the substrate consumed is not significant until the cells reach a high population level. When other readily utilizable organic compounds are present in the system, the acclimation period may be caused by diauxic utilization of substrate by microorganisms. The length of the acclimation period will vary with the structure and concentration of the test chemical, the chemical compositions of the water, the types and numbers of organisms present, and other environmental conditions.

Monod kinetics is applicable if the lag period is caused by too low a microbial inoculation (Braun and Berthauex, 1970); mathematical treatment is difficult if acclimation is caused by physiological adjustments of the microbial community. A biodegradation rate constant can be obtained when the acclimation period is over and when the microorganisms are actively consuming the chemical. However, when a chemical is first released into a place where no previous history of exposure exists, the time required for acclimation cannot be ignored. This information can be obtained through the river die-away type of test with various water bodies.

Concentration of Test Chemical

The concentrations of test chemicals to be used are decided by realistic pollution levels, solubilities, toxicities, and sensitivity of analytical procedures. As expressed in Monod kinetics, the initial substrate concentration in the growth media will affect the specific growth rate, and the substrate utilization rates are slower at low substrate concentrations. Low chemical concentrations also affect acclimation periods and extents of degradation (Pfeil and Lee, 1968). At too low concentrations, high-adsorption compounds may not have enough "available substrate" for microorganisms to grow. Certain microorganisms are apparently totally unable to grow when their organic carbon sources are present in minute concentrations (Alexander, 1973; Boethling and Alexander, 1979). At high substrate concentrations, the Monod equation predicted that the degradation rates are independent of substrate concentration. Many chemicals are, however, toxic or inhibitory at high concentrations, which decrease the utilization rate through inhibition of enzyme action, repression of enzyme production, inhibition of microbial growth, or killing of the organisms. Edwards (1970) discussed mechanisms causing substrate inhibition and used them to derive five mathematical models.

Additional Organic Compounds

The presence of additional organic compounds in the test media may either enhance or repress the biodegradation of testing compounds in several different ways. For instance, some extra organic compounds may provide energy and carbon for microorganisms to grow extensively and increase both the biomass of microbes responsible for the biodegradation and the utilization rate. They may also increase the growth of nonrelated organisms. Monod kinetics will be hard to apply under these conditions, since the equation is for the growth-limiting substrate concentrations with regard to cultures responsible for degradation.

The additional organic compounds may be an essential nutrient for the microorganism. A compound that is a structural analog of a test chemical may help induce enzyme(s) and reduce the acclimation period.

An additional compound may act as a cometabolic substrate for some compounds. Cometabolism is very important in biodegradation. This is a phenomenon in which an organic compound may be transformed only when another organic compound(s) is (are) present to serve as a carbon and energy source. This cometabolic substrate may be a structurally analogous compound or may be unrelated. For example, it was demonstrated that benzothiophene was not degraded unless naphthalene was also added to the inorganic nutrient media (Chou and Bohonos, 1979). Various mixed organic compounds are present in the natural environment, and very often pollutants from industrial plants are mixtures of compounds of which many are chemically related. Thus, test procedures to evaluate the biodegradability of a specific chemical as a sole carbon source may often underestimate the rate of biodegradation versus the rate in a natural water or soil sample that contains many organic compounds capable of acting as cometabolites (Horvath, 1972).

The presence of readily metabolizable carbon sources may be preferentially utilized, cause catabolic repression or enzyme inhibition. Degradation of test chemicals may not take place until this extra carbon source is exhausted. This phenomenon is referred to as a diauxic process. The diauxic effect of glucose in mixed substrate on other compounds with heterogeneous mixed culture has been investigated extensively (Gaudy et al., 1964; Stumm-Zollinger, 1966; Sikka and Saxena, 1973). Even in a laboratory, the media prepared from distilled water may be contaminated with small amounts of organic compounds; although the concentrations are low, they may still be high enough to cause interference in growth rate studies when low concentrations of a test chemical are used with a low level of inoculum (e.g., methylparathion in Smith et al., 1978).

The possibility also exists that coexisting compounds or metabolites at appropriate levels may be toxic or mutagenic to biodegradation microorganisms.

Inorganic Salts

Microorganisms require elements other than carbon--such as nitrogen, phosphorus, sulfur, magnesium, and some trace elements--for their growth and functions. Some salts, such as phosphates, are added to media for their buffering capacities. Many different mineral salts media have been used in biodegradation studies. No attempts have been made to determine whether variations in the composition of the mineral salts medium affect the biodegradability of a chemical compound, but the effect is probably small (Howard et al., 1975).

For biodegradation studies on some compounds, modification of the protocol may be needed. For instance, phosphonate compounds are biodegraded only when these compounds serve as a phosphorus source for bacteria in phosphate-deficient media (Cook et al., 1978). In some studies on biodegradation of dibenzothiophene, the heterocyclic sulfur was the only supply of sulfur in the media (Hou and Laskin, 1975).

Dissolved Oxygen

Oxygen generally serves as the terminal electron acceptor in oxidation of chemical compounds. Microorganisms are generally classified as obligatory aerobic, obligatory anaerobic, or facultatively anaerobic, depending on their requirements and sensitivity to molecular oxygen.

The presence or absence of dissolved oxygen will decide the types of microbial communities in the system. With low levels of organic compound and low microbial populations, occasional stirring of the media water may provide sufficient amounts of oxygen. With high microbial populations, extensive aeration is required. Generally, aerobic biodegradation of organic chemicals is faster and more extensive than anaerobic processes, but some compounds, such as chlorinated hydrocarbon pesticides, are more susceptable to biotransformation under anaerobic conditions (Hill and McCarty, 1967).

pH

All microorganism species have their optimum pH for growth and enzyme reactions. For most species the optimum is near neutral (pH 7) and they cannot grow in a strongly acidic or a strongly basic environment. Consequently, most biodegradations take place at a pH near neutral, although some organisms can grow in either an acidic or a basic environment and metabolize the substrate.

Changes in pH take place when microorganisms consume acidic or basic compounds or produce sufficient concentration of ionic metabolites. The pH is often maintained by adding buffer reagent to the test media.

Temperature

Temperature can also affect biodegradation in two ways: it can cause a change in individual physiological activities, or a change in population characteristics of mixed culture communities of microorganisms. Under specific conditions, each microbial strain has an optimum temperature for growth, which is not necessarily the optimum condition for each enzyme system or physiological action of the microbe. Generally, the higher the temperature, the more rapid is the biotransformation process. Biodegradations are very slow near freezing point. When the temperature rises to above the optimum, inactivation of enzymes and a decrease in the reaction rate result. Most organisms have optimal growth temperatures (and consequently, normal overall metabolic action) at temperatures from 20 to 37°C, but some thermophilic or psychophilic organisms would exhibit growth and/or survival at higher or lower temperature ranges.

A change in temperature will result in change in population and composition of the microorganisms in the mixed culture system.

The Arrhenius relationship may be applicable to express biodegradation rates as a function of temperature over narrow ranges (Moe, 1970). However, this expression does not apply to the ranges above optimum temperature and changing population of a mixed culture.

6.7.4 A Review of Aquatic System Biodegradability Tests

Test procedures for conducting biodegradability tests have varied considerably in equipment used, conditions controlled, and complexity of operations. As discussed earlier, numerous factors may affect biodegradation. Attempts have been made to simulate many different environmental conditions. Generally, there are two major types of test--static tests, which simulate natural water systems; and dynamic tests, which simulate biological wastewater treatment plant systems.

Typical methods include the river die-away test, the shaker flask test, the continuous and semicontinuous activated sludge tests, and the model ecosystem. Some of them use a simple glass container, but others use highly complex, continuous culture equipment. A review of the state of the art in biodegradation methods was made by Howard et al. in 1975.

River Die-Away Test

This test has been used by many investigators because of its simplicity and cost efficiency. It involves collection of raw water from rivers, lakes, or other natural water bodies, addition of a test chemical to the water, and analysis of water samples at various intervals for disappearance of the parent compound or the product(s) formed. The microbial populations are generally low, varying with the site and the season of collection. The container used may be a 1-liter mason jar, a 4-liter glass bottle, or a 5-gallon carboy bottle. The water sample used may vary from less than 1 liter to 20 liters. The incubation time for the sample may range from a few days to 8 weeks, depending on time of acclimation and rate of biodegradation of the test chemical. The containers are mixed and aerated by periodic shaking, magnetic stirring, or sparger aeration.

The water samples vary in chemical and microbial compositions, with the site or time of sampling in the same water body and with different water bodies. However, the river die-away test is the closest simulation of biodegradation conditions in natural aquatic environments.

The test, originally described by Hammerton (1955) in a study of sodium lauryl sulfate, is employed by many investigators who use water samples as microbial sources and growth media. Other investigators have added microorganisms for faster biodegradation; for example, natural water has been seeded with activated sludge (Garrison and Matson, 1964), centrifuged sewage effluent or river water (Hitzman, 1964). Others have added a pH buffer or extra nutrients (Sheers et al., 1967; Smith et al., 1977).

In some procedures, defined synthetic media have been used to minimize the variability of the water components; in this case, the sewage or natural water microorganisms are inoculated into the test media (Bunch and Chambers, 1967; British STCSD, 1966). One special method of doing this is the Biochemical Oxygen Demand (BOD) test, which measures dissolved oxygen consumption (APHA, 1971).

Shaker Flask Test (SF)

In this test, microorganisms from natural sources are inoculated into shaker flasks containing basal salts media with test chemicals. The media are standardized to use defined nutrients, thereby reducing the variability of the chemical components found in natural water. The flasks used range from 250 ml to 2 liters in volume. Sources of inocula used are water, activated sludge, sewage, soil, air-dried or lyophilized sludge, and air microbes. Acclimated cultures developed by the shaker flask test, the river die-away test, or the activated sludge test are used with the shaker flask method to study the degree or rate of degradation (Smith et al., 1977; SDA, 1965; Paris et al., 1975).

The flasks are normally aerated in shaker incubators, water samples are withdrawn periodically, and degree of biotransformations are determined. Gledhill (1975) used flasks equipped with $^{14}CO_2$ traps for ultimate biodegradation as well as for primary biodegradation studies.

The Soap and Detergent Association (SDA, 1965) adopted the shaker flask method for a presumptive test of biodegradability of detergents. The seed was adapted by making two 72-hour transfers, then conducting the test in the third generation of flasks. The Organization for Economic Cooperation and Development (1976) also adopted the shaker flask method for a screening test without adaptation.

Swisher (1968) used a 2-week transfer for the shaker flask adaptation and degradation studies because a 72-hour or a weekly transfer was too short for some compounds that were tested.

Continuous Flow Activated Sludge (CAS) System

There are many kinds of equipment that attempt to simulate different types of biological treatment plant conditions, or biodegradation in water containing high microbial populations that are continuously fed with chemical compounds and other nutrients, organic and inorganic. In general, such equipment consists of either a reactor that both agitates and aerates the material or a system that has separate aeration and settling compartments. One typical continuous system is the official method described by the German Government in 1962. The equipment consists of a 3-liter (working volume) aeration vessel and a sedimentation vessel that has a feeding rate of 1 liter per hour.

Swisher (1964) designed a miniature continuous-flow vessel that can operate in a much smaller space and requires smaller amounts of feed.

Semicontinuous Activated Sludge (SCAS) System

In this procedure, the feed is added periodically rather than continuously. The operation is a fill-and-draw process. A typical procedure is that used by the SDA (1965) as a confirming test. Detergent in synthetic nutrient solution is fed into an aerated vessel; after 23 hours of aeration, the mixture is allowed to settle and the supernatant is removed. New feed is then added and the process is repeated. Synthetic "sewage" normally includes organic nutrients.

Nitrilotriacetic acid was the sole carbon source in the SCAS method used in studies by Swisher et al. (1967).

Pitter (1976) used a 1-liter cylinder as semi-continuous activated sludge equipment to adapt microorganisms for the die-away type of biodegradation test. The SCAS method is used by some investigators as an adaptation procedure for seed to be used in biodegradation studies (Maurer et al., 1974).

Various other systems, such as trickling filters, septic tanks, and cesspools are used to study aerobic and anaerobic biodegradation.

Official Procedures for Testing Detergents

Most of the early aquatic chemical biodegradability tests were concerned with household detergents. Because of their widespread use and the large amounts involved, standard testing methods for such detergents have been adopted in many countries. In the U.S., the Subcommittee on Biodegradation Test Methods of the SDA in 1965 adopted a two-step biodegradation procedure for anionic surfactants alkyl benzene sulfonate and linear alkylate sulfonate. The shaker flask technique is used as the presumptive test and the SCAS method is used for a confirming test. The tests are conducted at $25^{\circ} \pm 3^{\circ}$ C. In the shaker flask test, the chemical is considered to be adequately biodegradable when monitoring by methylene blue colorimetric analysis on the 7th and 8th days if the 3rd-transfer flask shows 90% elimination from 30 mg/liter; less than 80% elimination is not considered to be adequately biodegradable. If reduction of surfactant is between 80 and 90%, its biodegradation must be confirmed by another test. In the confirmatory test (the SCAS test), the material (20 mg/liter) must be degraded by at least 90% to be considered adequately biodegradable. This two-step degradability test is a fail-safe type and does not provide the data for rate of biodegradation. The two 72-hour adaptations in shaker flasks may be justified for testing the adequacy of biodegradation of a surfactant, but some compounds require longer acclimation periods (Garrison and Matson, 1964; Swisher, 1968; Rogers and Kaplan, 1974). The 24-hr fill-and-draw SCAS method may not exactly simulate a sewage treatment plant, but it requires smaller amounts of feed, simpler equipment, and less labor than does the continuous method.

The West German Government in 1962 adopted a continuous sludge system for testing anionic surfactant, in which synthetic sewage (organic medium) containing 20 ppm methylene blue active surfactant was fed at 3-hour retention-time rates. Biodegradability was based on percent removal of methylene blue active surfactant between influent and effluent. This method more closely simulates sewage treatment plant operation. However, it requires a long operation period, bulky equipment, large volumes of feed, and a high labor cost. Another disadvantage to its use is the difficulty in maintaining stable biochemical operations and satisfactory circulation of sludge (Stennett and Eden, 1971).

The British Standing Technical Committee on Synthetic Detergents (STCSD, 1966) recommended a sludge die-away type of rapid screening test for anionic surfactant. The method used air-dried activated sludge as an inoculum, which was incubated with BOD dilution water containing the detergent (20 mg/liter). Aeration was by gentle stirring or by blowing air across the surface of the liquid. This method is an attempt to use standardized medium to reduce the variability of the river die-away test.

The Organization for Economic Cooperation and Development (OECD, 1971, 1976) adopted a shaker flask method for a screening test (static test) and a continuous activated sludge method for confirmatory test (dynamic test) to determine biodegradability of anionic and nonionic surfactants. In a shaker flask, medium containing mineral salts and the surfactant (5 mg/liter) is inoculated with mixed aerobic microorganisms (preferably activated sludge) and incubated on the shaker for up to 19 days at 25° C. The final percentage degradation is that obtained when the degradation curve reaches a plateau, or at the 19th day, whichever is earlier. "Soft" and "hard" anionic standards are used as references. The activated sludge method is the official German method, except that filtered activated sludge is used as the inoculum. The anionic surfactants (20 mg/liter in synthetic sewage) are measured by methylene blue colorimetry; the nonionic surfactants (10 mg/liter) are measured by precipitation with tetraiodobismuthate.

Comparison of Test Results

Cook (1968) compared the results of biodegradability tests of several different alkyl benzene sulphonates (ABS) by the bottle die-away test, the SDA shaker culture test, the official German method, the SDA-SCAS method, and the recirculating filter method. The SCAS and recirculating filter methods gave maximum results, and the German method generally gave the lowest results. The bottle die-away and shaker culture tests yielded average and similar removal percentages.

Truesdale et al. (1969) studied British STCSD die-away tests, the official German test, the SDA-SCAS test, and the recirculation filter test and compared these with a pilot-scale percolating filter method. The die-away method gave a high percentage of removal for "soft" anionic materials, compared to other methods, but the percentage was low for "hard" or "slow to acclimatize" ABS. Similar results were obtained with the official German method. The SCAS and recirculating filter methods yielded higher results.

Mausner et al. (1969) described the results of interlaboratory biodegradability testing of several nonionic surfactants by SDA member companies. After testing several different methods, they concluded that the SCAS type seems to be the best approach because of its higher reproducibility, but that no single standard method existed at that time for all types of nonionic surfactants. They attributed part of the problem to lack of a good general analytical method.

The reproducibility of the river die-away test was studied by Weil and Stirton (1964), using several anionic and nonionic surfactants. Sodium dodecanesulfonate was used as a standard to check the biological activity of river water samples. They tested five samples taken from the same spot in the Schuylkill River at various times. Except for one sample taken after a severe summer drought, all the curves of disappearance of the chemical versus time were nearly the same. In tests of waters from three diferent rivers, biodegradation appeared to proceed at about the same rate.

Setzkorn et al. (1964) presented data showing reproducibility of linear alkylate sulfonate (LAS) in various river waters and in various samples of Mississippi River water. They also reported large differences between C_{10}, C_{12} and C_{14}, C_{16} LAS in the adaptation period; however, when the compounds were readded to the water at 95% degradation time, their degradation rate was not significantly different.

Borstlap and Kortland (1967) pointed out that with the river die-away test, data can be obtained on adaptation time, biodegradation rate, and the amount of surfactant residue (if degradation is not complete). In tests with alkylaryl sulfonate surfactants, the degradation curves showed that some surfactants had different adaptation times but comparable degradation rates.

The Office of Toxic Substances, EPA, is preparing guidelines for premanufacture testing of new chemical substances (1979). The EPA has also tentatively proposed biodegradation test methods for assessing persistence of a chemical substance in a natural environment. The methods include the shaker flask method, the CO_2 evolution test, the BOD test, the SCAS method for aerobic biodegradation, and the methane and CO_2 production test for anaerobic biodegradation. The recommended acclimation method for shaker flasks is several 48- to 72-hour transfers, up to 13 days. These biodegradations are monitored by disappearance of dissolved organic carbon (DOC), CO_2 and/or methane evolution and uptake of oxygen. Although the proposed methods are the best available, being simple and low in cost, they may have some drawbacks when used in biodegradation rate studies. The evidence for biodegradation is indirect and no information of disappearance of the parent compound is obtained. The 48- to 72-hour transfers may be too short for chemicals requiring long adaptation periods. In the SCAS method the SDA confirmatory method is used for acclimation and screening tests; then the acclimated sludge is used for the degradation rate study with inorganic salts and the die-away operation. The test chemical is added at levels up to 100 and 200 mg/liter as a total organic carbon because DOC is used for the measurement. This high test concentration may not be applicable to many organic compounds that have low solubilities or high toxicities.

Biodegradation Rate Studies

Most biodegradability studies in the literature are qualitative in nature. The investigations were undertaken a) to determine whether biodegradation took place, b) to isolate microorganisms responsible for the biodegradation, and c) to use these isolates to study the metabolic pathways. Generally, quantitative studies were not made to obtain degradation rates and kinetic constants. Research is needed for quantitative measurement of biodegradation so that the rate constant can be used for assessment of the environmental fate of chemicals.

Mathematical expression was first empirically obtained by Monod (1949) to relate microbial growth rate to growth-limiting substrate concentration with a pure culture. Some modifications have been proposed (Contois, 1959; Powell, 1967) and different expressions have been used (e.g., Kono, 1968; Verhof et al., 1972). The Monod kinetics have also been applied to sewage treatment systems (Benedick and Horvath, 1967; Gaudy and Gaudy, 1967; Jones, 1973). Several attempts have been made to use substrate disappearance curves in batch systems to determine values for Xo, K_s, and μ_m. Knowles et al. (1965) applied the computer method, Gates and Marlar (1968) applied the graphical method, and Stratton and McCarty (1967, 1969) applied both methods. Rapid measurement of K_s with soluble substrates was proposed by Williamson and McCarty (1975).

Uptakes of organic substrates such as glucose and organic acids were measured by adding ^{14}C-labeled compounds to marine water or lake water samples, incubating for definite periods of time, and determining the amount of labeled carbon contained in the cells. Although the relation between the substrate concentrations and uptake rates is a hyperbola similar to the Michael-Menton equation (Parsons and Stickland, 1962; Wright and Hobbie, 1965; Vacarro and Jannasch, 1967; Robinson et al., 1973), the amounts of labeled carbon in the cells differ from the amounts of parent compound metabolized (Hamilton and Austin, 1967).

Eichelberger and Lichtenberg (1971) studied the persistence of 28 common pesticides in river die-away testing over an eight-week period at a concentration of 10 μg/liter. They determined the relative persistence of these pesticides; however, the samplings were not frequent enough to obtain degradation curves for a rate study.

Pitter (1976) adapted microorganisms in the SCAS method and used them to study the degree and rate of biodegradation of 123 organic compounds in terms of chemical oxygen demand (COD). The test chemicals were used as the sole carbon source in the batch test system, which contained 200 COD/liter, with 100 mg of dry matter/liter of adapted sludge as inoculum. The rate of degradation was expressed in mg of COD removed by 1 gram of the initial dry matter of inoculum per hour. Moe (1970) used the modified Stratten and McCarty (1967) equation of the Monod expression to obtain degradation constants for isopropyl carbanilate and isopropyl *m*-chlorocarbanilate.

Paris et al. (1975) applied the Monod equation in a biodegradation study of malathion. Several low levels of the pesticide in flasks were inoculated with washed, acclimated, mixed microorganisms. The second-order biodegradation rate constant kb_2 obtained was compared with the value calculated from the μ_m, K_s, and Y obtained. They found that these values were in agreement at low bacterial and malathion concentrations. They also applied this method to obtain second-order constants for biodegradations of the butoxyethyl ester of 2,4-dichlorophenoxyacetic acid (2,4-D) and Methoxychlor.

Smith et al. (1977, 1978) studied chemical transportation, chemical transformation, and biodegradation of 11 compounds, obtained rate constants of each pathway, and used these values in a computer model to predict the fate of the chemicals in ponds, rivers, and lakes. Biodegradation studies of several water samples were first conducted with river die-away type screening tests in aerated bottles. Once biodegradation took place, acclimated cultures were enriched in shaker flasks and transferred; one of the enriched mixed systems was used for a rate study for each chemical. One or more methods, including batch biodegradation with low level of inoculum, continuous culture method, and batch biodegradation with high populations of microbes and low substrate concentrations, were used to obtain rate constants for p-cresol, quinoline, benzoquinoline 9H-carbazole, and dibenzothiophene.

Paris et al. (1978 and 1981) collected several waters from rivers and ponds and conducted the river die-away test with the butoxyethyl ester of 2,4-D, Malathion, and Chloropham to study the variability of different waters. The amount of pesticides used was less than 1 mg/liter, and bacterial and pesticide concentrations were monitored. Due to low concentrations of substrate added, the investigators found no significant change in the bacterial populations caused by the metabolism of the pesticides. Malathion and 2,4-D ester were readily hydrolyzed. Chloropham required long acclimation periods. The degradation curves were pseudo-first order. Although bacterial populations are very different, the second-order rate constant calculated from the curves and bacterial counts showed that variation of rate constants among the natural waters were small.

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CHAPTER 7. VOLATILIZATION FROM WATER

by

J. H. Smith and D. C. Bomberger

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7. VOLATILIZATION FROM WATER

7.1 INTRODUCTION

Volatilization of a chemical that is dissolved in a water body is the transport of the chemical from the water body to the atmosphere. The concentration of the chemical in water decreases even though a transformation does not occur, but the water body serves as an "area source" of emission of the chemical to the atmosphere. Thus, while the exposure of the aquatic environment to the chemical decreases, the exposure of the air environment increases. However, the amount and rate of dilution of the chemical in the air may be so fast that the atmosphere exposure is not a significant hazard.

Current evidence suggests that volatilization is likely to be the major aquatic fate of low molecular weight, nonpolar compounds that are not rapidly biodegraded or chemically transformed. Volatilization rates of higher molecular weight compounds can also be significant under certain conditions. The protocols of this chapter represent the current state of the art methodology for predicting the volatilization rates of chemicals in aquatic environments. The background section is a critical review of the bases for the proposed methods.

7.2 SUMMARY

Screening and detailed laboratory test protocols for volatilization of chemicals have been prepared to enable the investigator to estimate the volatilization rate constants and half-lives of chemicals in several representative water bodies. Only chemicals with half-lives of less than three months in small rivers are considered for detailed studies.

The test protocols are based on an extensive body of chemical, chemical engineering, limnological, and oceanographic literature on mass transport phenomena. The screening studies are made by predicting the volatilization rate constant from the physical and chemical properties of the chemical. The recommended protocols for the detailed tests are cost-effective and simple to use for a wide range of chemicals.

The screening tests for volatilization of the chemical from water require data for the following physical properties: melting or boiling point, solubility in water at 20°C, vapor pressure at 20°C (which can often be estimated), and, if possible, the Henry's law constant. The heat of fusion is usually required for solids, if the Henry's law constant has not been measured. These data, plus the chemical structure, are used to estimate the volatilization rate constant.

The protocols for the detailed laboratory tests require first that the compound be classified as a low or high volatility compound, which is done on the basis of the screening test. For high volatility compounds, the ratio of the volatilization rate constant of the chemical, k_v^C , to the oxygen reaeration rate, k_v^O, is measured over a range of stirring rates. Then, since values of k_v^O for representative water bodies are available, k_v^C in the environment can be calculated, since

$$(k_v^C)_{env} = (k_v^C/k_v^O)_{lab}\ (k_v^O)_{env} \tag{7.1}$$

Similarly, for low volatility compounds, the ratio of k_v^C to k_v^O and the gas-phase mass transport coefficient for water, k_g^W, is measured at several stirring rates. Then, k_v^C in the environment is

$$\left(k_v^C\right)_{env} = \left(\frac{k_v^C}{k_g^W}\right)_{lab} \frac{L_{lab}}{L_{env}} \left(k_g^W\right)_{env} \tag{7.2}$$

where L_{lab} is the solution depth of the laboratory apparatus and L_{env} is the depth of the water body. These procedures are applicable to any well-mixed water body for which the values of k_v^O and k_g^W can be estimated.

7.3 CONCLUSIONS

The present knowledge of the theory and experimental aspects of volatilization of high volatility compounds when liquid phase mass transport resistance controls the volatilization rate provides a sound basis for the recommended protocols. These protocols have been evaluated in our laboratories during several research programs. However, the protocol for medium and low volatility compounds are based on our assessment of the theoretical aspects of volatilization when gas phase mass transport limits the overall volatilization rate plus preliminary laboratory validation studies. These procedures have not been adequately verified in the laboratory. In both cases, the laboratory measurements are relatively simple to perform and require common laboratory equipment.

The screening test protocol can be used to determine if the chemical should be classed as high or low volatility. It can also be used to calculate, with good accuracy, the volatilization rate constant ratio, k_v^C/k_v^O. Values of k_v^C/k_g^W for low volatility compounds can be estimated, but the accuracy of the estimation procedure is known for only a few chemicals.

The detailed test protocols can be used to measure k_v^C/k_v^O and k_v^C/k_g^W with good accuracy and precision in the laboratory. The accuracy of the predicted values of $(k_v^C)_{env}$ depends on the accuracy of the literature or estimated values of $(k_g^W)_{env}$ or $(k_v^O)_{env}$ for the specific water body. The techniques are excellent for estimating $(k_v^O)_{env}$ for streams and rivers. The corresponding procedures are inadequate for ponds and lakes.

7.4 RECOMMENDATIONS

The protocol recommended for medium and low volatility compounds should be subjected to an extensive laboratory validation program. Measurements of k_v^C, k_v^O, and k_g^W should be made at several temperatures, stirring rates, and wind velocities.

The techniques for predicting k_v^O in ponds and lakes and k_g^W in streams and rivers should be reviewed. Field studies should be devised and carried out to validate the procedures.*

7.5 SCREENING TESTS

7.5.1 Purpose

This screening test protocol is intended to classify chemicals as high, medium, or low volatility and to identify chemicals with volatilization half-lives of less than three months.

7.5.2 Procedure

The following physical property data for a chemical must be available or measured before proceeding with the screening test.

- Melting point (T_m, °C)
- Solubility in water at 20°C (C_{sat}, g liter^{-1} and mole liter^{-1})

Either

- Henry's law constant, at 20°C (H_c, torr liter mole^{-1})†

or

- Vapor pressure at 20°C (P_v, torr)
- Heat of fusion, if the chemical is a solid at 20°C and if the vapor pressure data used to calculate H_c (next section) is for the liquid (ΔH_f, cal mole^{-1}).

The screening test consists of calculating the value of the Henry's law constant, H_c, which is used to determine if the environmental half-life for volatilization is less than about three months.

Henry's law is expressed as

$$P^C = H_c[C] = H_c C_W \tag{7.3}$$

where P^C is the partial pressure (in torr) of the chemical C above an aqueous solution (that is, at or below the solubility limit of the chemical) at a concentration $[C] = C_W$ (in moles liter^{-1} *= M). Then H_c is the Henry's law constant expressed in units of torr M^{-1}.*

---

*A series of aromatic compounds, such as naphthalene, anthracene, pyrene, and benz[a]anthracene, are being studied at SRI under a grant from the National Science Foundation.

†If a measured value of the Henry's law constant of the chemical in water is available, the calculation steps should be omitted.

The value of H_c for a gas is obtained by measuring solubility of the gas in water at several partial pressures. Then H_c is the slope of a plot of the partial pressure (torr) versus its concentration of C in solution (M) (plotted as the abscissa) as the concentration approaches zero, using a graphical method. If measurements of gas solubility are required, the reader is referred to the review by Mader and Grady (1971) for specific measurement techniques.

The value of H_c at 20°C can be measured (Mackay et al., 1979) or estimated from the vapor pressure and the solubility in water, using equation (7.5)

$$H_c = P_v^C / C_{sat} \tag{7.5}$$

where P_v^C is the vapor pressure of pure C and C_{sat} is the solubility of pure C in water (M) at 20°C, provided the values of P_v^C and C_{sat} are for the same phase (both solid or both liquid).

If the vapor pressure of the chemical is available only at some temperature other than 20°C, the integrated form of the Clausius-Clapeyron equation

$$P_1 = P_2 \exp\left[\frac{\Delta H_v}{1.987}\left(\frac{1}{T_2} - \frac{1}{293}\right)\right] \tag{7.6}$$

can be used to estimate the vapor pressure at 20°C provided there is no phase change; P_2 is the vapor pressure at temperature T_2 (K), P_1 is the vapor pressure at 293 K, and ΔH_v is the heat of vaporization (cal mole^{-1}). This extrapolation may not be accurate over a wide temperature range. Therefore, if possible, the vapor pressure should be measured at 20°C. Methods for measuring vapor pressure (Thomson and Douslin, 1971) and solubility (Mader and Grady, 1971) have been reviewed.

If the chemical is a solid at 20°C and the vapor pressure data at T_2 are for the liquid phase of the chemical

---

* An alternative definition of Henry's law, which is often used, is

$$C_g = H\, C_W \tag{7.4}$$

where C_g is the concentration of the chemical in the gas phase. In this case, C_g and C_W are expressed in the same units of concentration, such as g liter^{-1}, and H is unitless. Other units of H, such as torr and atm m^3 mole^{-1} can be used, provided appropriate units for the partial pressures and concentrations in the liquid are also used.

$$H_c = \frac{P_{2\ell}}{C_{sat}} \exp\left[\frac{\Delta H_v}{1.987}\left(\frac{1}{T_2} - \frac{1}{293}\right)\right] \exp\left[\frac{\Delta H_f}{582.2}\left(\frac{293}{T_m} - 1\right)\right] \qquad (7.7)$$

where $P_{2\ell}$ is the vapor pressure of the chemical in the liquid phase at temperature T_2, T_m is the melting point (K), and H_f is the heat of fusion (cal mol^{-1}), which is easily measured with a differential thermal analyzer.

The volatilization behavior of a chemical can be divided into three classes that depend on the value of H_c. These are:

- High volatility: $H_c > 1000$ torr M^{-1}
- Intermediate volatility: $10 < H_c < 1000$ torr M^{-1}
- Low volatility: $H_c < 10$ torr M^{-1}.

Volatilization is likely to be an important environmental fate for chemicals that fall into the high and intermediate volatility classes. In these cases, detailed studies should be carried out. The case of low volatility compounds is not as clearcut.

In Section (7.7.6) it is shown that if H_c is greater than about 2 torr M^{-1}, the half-life for volatilization of the low volatility compound may be less than about 3 months. If screening studies suggest that other processes, such as photolysis and biodegradation, are slow, detailed volatilization rate studies should be carried out. Clearly, the researcher must exercise careful judgment in deciding if detailed volatilization studies are needed if H_c is between 0.5 and 10 torr M^{-1}.

7.6 DETAILED STUDIES

7.6.1 Purpose

This detailed test protocol is intended to provide estimates of the volatilization rate constant of a chemical from typical natural water bodies.

7.6.2 Procedure for High Volatility Compounds

Introduction

The basis of the test procedure for high volatility compounds is the measurement of the ratio of the volatilization rate of the chemical to the oxygen reaeration rate constant, k_v^C/k_v^O.

The oxygen reaeration rate, R_v^O, is

$$R_v^O = \frac{d[O_2]}{dt} = -k_v^O\left([O_2]_s - [O_2]_t\right) \qquad (7.8)$$

where k_v^O is the oxygen reaeration rate constant, $[O_2]_s$ is the concentration of oxygen at saturation and $[O_2]_t$ is the oxygen concentration at time t.

The volatilization rate of the chemical, R_v^C, is defined by

$$R_v^C = \frac{d[C]}{dt} = -k_v^C[C]_t \qquad (7.9)$$

where k_v^C is the volatilization rate constant of the chemical and $[C]_t$ is the concentration of the chemical in moles liter^{-1} (M).

The value of k_v^C in the environment $(k_v^C)_{env}$, can be calculated, provided estimates (or measurements) of $(k_v^O)_{env}$ for the specific water body are available, since

$$(k_v^C)_{env} = (k_v^C/k_v^O)_{lab}\,(k_v^O)_{env} \qquad (7.1)$$

Apparatus

The recommended apparatus, which is shown in Figure 7.1, consists of a 2-liter beaker modified with two 0.635-cm (1/4-in.) O.D. tubing connections at the bottom. The probe of the dissolved oxygen analyzer is mounted in a glass holder to maximize the flow velocity past the membrane and minimize the hold-up volume. The water is circulated past the oxygen probe with a small pump. The Cole Palmer All-Teflon metering pump No. 7180 is recommended because it is all Teflon; other pumps might be satisfactory. The aqueous solution is stirred with a constant-speed stirring motor, such as Scientific Products Catalog No. 47980-1 equipped with a propeller stirrer. Close temperature control is not required because the value of k_v^C/k_v^O is independent of temperature, within experimental error (Smith et al., unpublished results).

Calibration of the Apparatus

The relationship between k_v^O and the stirring rate for the system should be determined before measurements of k_v^C/k_v^O are made. The procedure is as follows. Calibrate the dissolved oxygen analyzer in air, according to the manufacturer's instructions. (This calibration is not critical, since the instrument is recalibrated at the end of the experiment.) Place the probe of the dissolved oxygen analyzer in the glass holder. Fill the beaker with about 1600 ml of distilled water. Start the recirculation pump. Purge the oxygen from the water using reagent grade nitrogen, which is bubbled through a glass frit on the end of a long glass tube that has been placed at the bottom of the beaker. Monitor the decrease in the oxygen concentration with the dissolved oxygen analyzer. When the oxygen concentration is less than 1.5 ppm, remove the sparger and start the stirrer motor. Adjust the stirring speed to a preset value, which can be the revolutions per minute or an arbitrary setting on the motor speed controller. Begin monitoring the oxygen concentration as a function of time. At least 15 observations of the oxygen concentration $[O_2]_t$ should be taken, and the dissolved oxygen concentration should be greater than 8 ppm before the experiment is ended. At the end of the experiment, increase the stirring speed and allow the oxygen concentration to reach a constant value, $[O_2]_s$ and note this value.

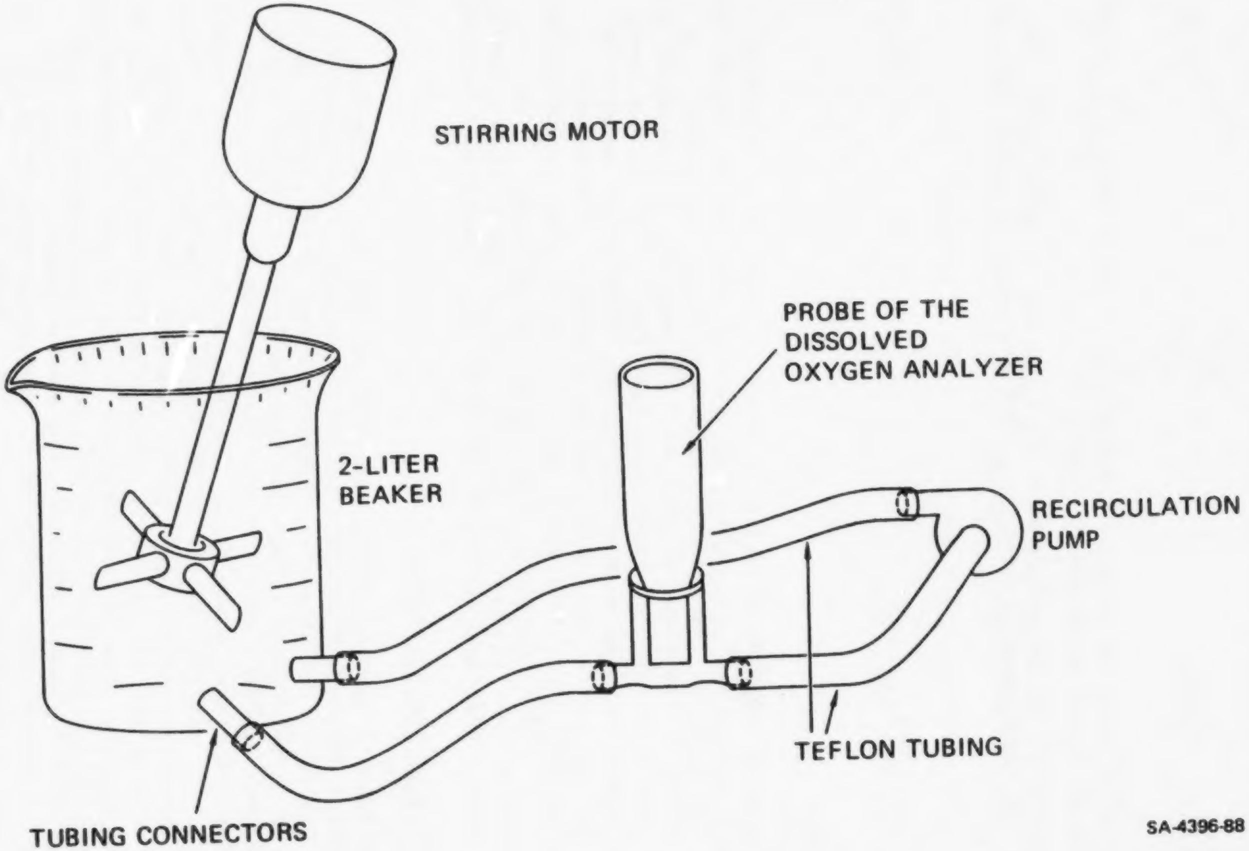
STIRRING MOTOR
PROBE OF THE DISSOLVED OXYGEN ANALYZER
2-LITER BEAKER
RECIRCULATION PUMP
TEFLON TUBING
TUBING CONNECTORS
SA-4396-88

FIGURE 7.1 VOLATILIZATION RATE APPARATUS FOR HIGH VOLATILITY COMPOUNDS

A plot of log ($[O_2]_s - [O_2]_t$) versus t (in hours) should be a straight line. The slope of this line is $-0.434\ k_v^O$. The value of k_v^O is calculated using a linear least squares analysis of the data, which is described in the Data Analysis subsection below.

It should be possible to choose stirring rates with this apparatus that give k_v^O values between 1 and 15 hr^{-1}. A plot of k_v^O versus stirring rate should be prepared for the convenience of the operator.

Measurement of k_v^C/k_v^O.

A stock solution of the chemical in methanol or acetonitrile should be prepared. The concentration of the chemical in the stock solution should be adjusted so that a dilution of 0.1 ml to 1 liter of water will give a concentration of the chemical in water that is at least 10 times the detection limit but is less than 50 ppm and less than about one-half of the solubility limit of the chemical in water.

Calibrate the dissolved oxygen analyzer in air, according to the manufacturer's instructions. (This calibration is not critical, since the instrument is recalibrated at the end of the experiment.) Place the probe of the dissolved oxygen analyzer in the glass holder. Fill the beaker with about 1600 ml of distilled water. Start the recirculation pump. Purge the oxygen from the water using reagent grade nitrogen, which is bubbled through a glass frit on the end of a long glass tube that has been placed at the bottom of the beaker. Monitor the decrease in the oxygen concentration with the dissolved oxygen analyzer. When the oxygen concentration is less than 1.5 ppm, add the chemical to be studied in the stock solution. No more than about 0.16 ml of stock solution should be added to the water.

Start the stirring motor at the preselected speed. Remove the sparger and start the stirrer motor. Adjust the stirring speed to a predetermined value which can be the revolutions per minute or an arbitrary setting on the motor speed controller. For convenience, the initial runs should be made at stirring speeds that give k_v^O values of approximately 2 to 5 hr^{-1}. Begin monitoring the oxygen concentration with the dissolved oxygen analyzer, and withdraw aliquots of the solution for analysis of the chemical. If the withdrawn aliquots are not analyzed immediately, they should be stored in the refrigerator in sealed containers without headspace and should not be poured from container to container to minimize losses by volatilization.

Two criteria for data collection should be met. At least 10 measurements of the concentration of the chemical, $[C]_t$, should be made. The final concentration of C should be less than 25% of the initial concentration. Also, at least 15 observations of the oxygen concentration $[O_2]_t$, should be made, and the dissolved oxygen concentration should be greater than 8 ppm before the experiment is ended by increasing the stirring speed. At the end of the experiment, increase the stirring speed and allow the oxygen concentration to reach a constant value, $[O_2]_s$, and note this value.

This experiment should be repeated at least six times at stirring rates corresponding to a range of k_v^O from about 1 to 15 hr^{-1}.

Data Analysis

Estimation methods for error analysis of the test protocol are based on certain assumptions concerning the accuracy of specific measurements and relationship between variables. The test protocol for high volatility compounds proposed here requires measurements of concentrations of chemical and dissolved oxygen as a function of time from which the ratio k_v^C/k_v^O is calculated.

The estimate of the volatilization rate constant k_v^C is related to the measured variables, concentration and time, by the following regression equation

$$\hat{k}_v^C = \frac{n\Sigma(t)\ln C - \Sigma t \Sigma \ln C}{n\Sigma t^2 - (\Sigma t)^2} \tag{7.10}$$

where C is the concentration of chemical measured at time t and the hat signifies that $\hat{k}_v^C$ is an estimate of k_v^C. This version of the regression equation does not require that $\ln(C/C_o) = 0$ at $t = 0$; that is, the line is not forced through the origin and any significant departure from the origin indicates bias in the values of C at $t > 0$.

The intercept, C_o, the concentration at $t = 0$, is obtained from the equation

$$\ln\hat{C}_o = \frac{1}{n}(\Sigma \ln C - \hat{k}_v^C \Sigma t) \tag{7.11}$$

The preferred measurement of error in experiments of this kind is the 95% confidence limit, CL(95%)

$$CL(95\%) = t_{n-2,\alpha}\left\{\frac{\Sigma(\ln C)^2 - \ln\hat{C}_o\Sigma\ln C - \hat{k}_v^C(\Sigma \ln C)\Sigma t}{(n-2)\,[\Sigma t^2 - (\Sigma t)^2/n]}\right\}^{\frac{1}{2}} \tag{7.12}$$

where $t_{n-2,\alpha}$ is the t-statistic for n observations and $(1-\alpha)100$ confidence limit (%). (see Table 7.1).

Then, the confidence interval of k_v^C is

$$\hat{k}_v^C - CL < k_v^C < \hat{k}_v^C + CL \tag{7.13}$$

TABLE 7.1 VALUES OF $t_{n-2,5\%}$

	n										
	10	11	12	13	14	15	16	17	18	19	20
$t_{n-2,5\%}$	2.31	2.26	2.23	2.20	2.18	2.16	2.14	2.13	2.12	2.11	2.10

The simplest way to fit the data is to use the linear regression programs that are built into some hand-held calculators. The values of $\ln[C]_t$ are entered as the ordinate, y, and the time, in hours, is entered as the abscissa, x. The hand-held calculators will calculate the slope, $\hat{k}_v^C$, the intercept, $\ln C_o$, and the correlation coefficient for the data. The values for the terms $\Sigma(t)\ln C$, $\Sigma\ln C$, Σt and Σt^2 will be stored in the memory of the calculator and can be recalled to simplify the calculation of CL(95%). Least squares routines on larger computers could also be used.

The estimate of the oxygen reaeration rate constant $\hat{k}_v^O$ is calculated from the following regression equation:

$$\hat{k}_v^O = \frac{n\Sigma(t)[\ln(C_s-C)] - \Sigma t\Sigma\ln(C_s-C)}{n\Sigma t^2 - (\Sigma t)^2} \qquad (7.14)$$

where C_s and C have been substituted for $[O_2]_s$ and $[O_2]_t$ to simplify the notation. This version of the regression equation does not require that $\ln[(C_s-C)/(C_s-C_o)] = 0$ at $t = 0$; that is, the line is not forced through the origin and any significant departure from the origin indicates bias in the values of (C_s-C) at $t > 0$.

The intercept, (C_s-C_o), the oxygen deficit at $t = 0$, is obtained from the equation

$$\ln(C_s-\hat{C}_o) = \frac{1}{n}[\Sigma\ln(C_s-C) - \hat{k}_v^O\,\Sigma t] \qquad (7.15)$$

The preferred measurement of error in experiments of this kind is the 95% confidence limit, CL(95%):

$$CL(95\%) = t_{n-2,\alpha}\left\{\frac{\Sigma[\ln(C_s-C)]^2 - \ln(C_s-\hat{C}_o)\Sigma\ln(C_s-C) - k_v^C\,\Sigma t\Sigma\ln(C_s-C)}{(n-2)[\Sigma t^2 - (\Sigma t)^2/n]}\right\}^{1/2} \qquad (7.16)$$

Then, the confidence interval of k_v^O is

$$\hat{k}_v^O - CL < k_v^O < \hat{k}_v^O + CL \qquad (7.17)$$

Hand-held calculators can be used for these calculations by entering $\ln(C_s - C)$ for the ordinate y_i and t for the abscissa x_i.

Calculation of k_v^C/k_v^O

A plot of k_v^C versus k_v^O (abscissa), including the 95% confidence limits for each value of k_v^O and k_v^C from equation (7.16), is made. The best straight line is drawn through the data points, using a linear least squares fit forced through the origin.* Then an estimate of the average value of k_v^C/k_v^O can be calculated from

$$\widehat{(k_v^C/k_v^O)} = \frac{\Sigma(k_v^O)_j (k_v^C)_j}{\Sigma(k_v^O)_j^2} \qquad (7.18)$$

where the subscript j refers to the j th measurement of k_v^C/k_v^O. The 95% confidence limit on k_v^C/k_v^O, CL′, is

$$CL' = t_{n-1,\alpha}\left[\frac{\sum(k_v^O)_j^2 - \widehat{\left(\frac{k_v^C}{k_v^O}\right)}\sum(k_v^O)_j(k_v^C)_j}{(n-1)\ \Sigma(k_v^O)_j^2}\right]^{\frac{1}{2}} \qquad (7.19)$$

and

$$\widehat{\left(\frac{k_v^C}{k_v^O}\right)} - CL' < \frac{k_v^C}{k_v^O} < \widehat{\left(\frac{k_v^C}{k_v^O}\right)} + CL' \qquad (7.20)$$

Our experience has shown that the 95% confidence limits on the average value of k_v^C/k_v^O for high volatility compounds is about 5 to 10% of the magnitude of k_v^C/k_v^O.

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*Strictly speaking, a nonlinear least squares analysis, using all of the concentration versus time data should be used. However, this would be very expensive, and, in our experience, would not give substantially different values of k_v^C/k_v^O.

7.6.3 Procedure for Low Volatility Compounds

Introduction

The basis of the test procedure for low volatility compounds ($H_c < 10$ torr M^{-1}) is the measurement of the ratio of the volatilization rate constant of the chemical, k_v^C, to the water evaporation mass transfer coefficient, k_g^W. This ratio should be constant for low volatility compounds. The volatilization rate of low volatility compounds is limited by gas phase mass transport; therefore, the wind speed above the water body determines the rate. However, since in many cases the chemical may be either a low or intermediate volatility compound the ratio k_v^C/k_v^O is also measured at several water turbulence levels to provide an estimate of the liquid phase mass transport coefficient.

The rate constants k_v^C and k_v^O are defined by equations (7.8) and (7.9), respectively, in the previous section. The value of k_g^W (cm hr^{-1}) is estimated from

$$k_g^W = N_w\left(\frac{3464}{P_o^W - P^W}\right) \quad (7.21)$$

where N_w is the flux of water evaporating through the gas phase boundary layer and is measured as the weight of water lost per unit area per unit time (g cm^{-2} hr^{-1}), P_o^W is the vapor pressure of water (torr) at temperature T (K), and P^W is the partial pressure of water in the bulk gas phase (torr). Thus, values of k_g^W for both laboratory and environmental conditions can be calculated from measured values of N_w, provided average temperatures and relative humidities are also available. Then

$$\left(k_v^C\right)_{env} = \left(\frac{k_v^C}{k_g^W}\right)_{lab} \frac{L_{lab}}{L_{env}} \left(k_g^W\right)_{env} \quad (7.22)$$

Apparatus

The recommended apparatus consists of a 19 x 10 cm crystallizing dish, a constant speed stirring motor equipped with a propeller stirrer, a dissolved oxygen probe, a balance capable of weighing up to 8 kg at ± 0.5 g, and a 4-in. "muffin fan". The laboratory air temperature and relative humidity should be measured with a psychrometer.

Calibration of the Apparatus

The procedure for correlating the propeller stirring speed with k_v^O was given in Section 7.6.2. In this case, the stirring rate should be adjusted so that k_v^O is greater than 2 hr^{-1}. The balance is used to weigh the dish at regular time intervals to determine water loss rates. The muffin fan is located either 10 cm or 30 cm from the surface of the beaker, in a horizontal direction. The water loss rate should be measured at several stirring rates, without the fan and at the two fan locations to determine N_w under the various conditions. N_w should be nearly independent of the stirring rate (Mackay and Cohen, 1976).

Experimental Procedure

The procedure is designed to evaluate k_v^C, k_v^O, and k_g^W in the same experiment. The experimental plan is to determine the volatilization rate using three conditions: no fan, a fan at 10 cm, and a fan at 30 cm at a turbulence level that produces an oxygen reaeration rate constant of ~2 and ~15 hr^{-1} for each condition.

A method for analyzing the chemical in water must be developed. Chemicals in the low volatility class will either be very soluble in water or have both a low vapor pressure and a very low solubility in water; thus, special analytical techniques may be necessary. Also, if the solubility is less than about 40 μg $liter^{-1}$, problems with sorption of the chemicals to the apparatus and detection system may be encountered. Whenever possible, direct analysis of the aqueous solution is desirable.

In most cases, the value of k_v^C will be much less than that for k_v^O. In fact, the experiment may take several days. Therefore, the measurements of $[C]_i$ and the weight of the beaker, W_i, should be made at approximately t = 0, 0.5, 1, 2, 3, 4, 6, 8, 10, 15, 20, 30 and 40 hours. The change in weight of the crystallizing dish for the i^{th} time interval, $\dot{W}_i$, is

$$\dot{W}_i = W_i^o - W_i^t \tag{7.23}$$

where W_i^o is the initial weight of the crystallizing dish and W_i^t is the weight of the dish at time t. After the amount of water lost in the i^{th} time interval is measured, an amount of distilled water equal to $\dot{W}_i$ is added to the crystallizing dish. The solution is then stirred briefly, and an aliquot is withdrawn for analysis of the chemical. The concentration of the chemical is C_i. Measurement of T and the relative humidity should be made at the same time. Measurements of k_v^O, which will increase as the water evaporates, should be made at t = 0, 6, 20 and 40 hours. The speed of the stirring motor can be reduced slightly each time to maintain k_v^O approximately constant during the experiment. The depth of the vortex created by the stirrer should also be recorded.

The average value of k_g^W for each interval between weighings of the beaker is calculated. First, the wet and dry bulb temperatures of the laboratory air are used to calculate T_i, P_o^W, and P^W where T_i is the dry bulb temperature (converted to degrees K), P_o^W is the vapor pressure of water at the dry bulb temperature (torr), and P^W is the actual vapor pressure of water in the laboratory atmosphere (torr). The conversion of wet and dry bulb temperatures to vapor pressures of water is conveniently done by using standard psychrometry tables (for instance, see List, 1958). Then, for the i^{th} measurement (at each value of t)

$$k_{gi}^W = \frac{3464\ \dot{W}_i T_i}{A\ (P_o^W - P^W)_i} \tag{7.24}$$

where W is the weight of the beaker (g), t is the time of the i^{th} and $i+1^{th}$ measurement (hr), and A is the area of the surface of the water (cm^2). If the water surface is flat, A is

$$A = \pi r^2 \tag{7.25}$$

where r is the radius of the beaker (cm). However, if a vortex is formed, then the surface area of the vortex is approximated by the surface area of a cone

$$A = \pi r (r^2 + h^2)^{\frac{1}{2}} \tag{7.26}$$

where h is the depth of the vortex. The average value of k_g^W, $\overline{k_g^W}$, is

$$\overline{k_g^W} = \frac{1}{n} \Sigma k_{gi}^W \tag{7.27}$$

Both $\overline{k_g^W}$ and its standard deviation, $\sigma(k_g^W)$, can be calculated conveniently using hand-held calculators.

The concentration of chemical observed at each sampling, C_i, is used to calculate k_v^C, using equations (7.10-7.13). The value of k_v^C/k_g^W (which is k_v^C/k_g^W for the experiment and has units of cm^{-1}) is then calculated. This procedure should be repeated for at least six measurements at no fan, the fan at 10 cm and the fan at 30 cm and at least two liquid stirring speeds.

If the compound is in the low volatility class, then k_v^C/k_g^W should be nearly independent of k_v^O. Then an estimate of the average value of k_v^C/k_g^W can be calculated from

$$\widehat{(k_v^C/k_g^W)} = \frac{\Sigma (k_v^C)_j (k_g^W)_j}{\Sigma (k_g^W)_j^2} \tag{7.28}$$

where the subscript j refers to the j^{th} measurement of k_v^C/k_g^W. The 95% confidence limit on k_v^C/k_g^W, CL, is

$$CL = t_{n-1,\alpha} \left[\frac{\Sigma (k_g^W)_j^2 - \left(\widehat{\frac{k_v^C}{k_g^W}} \right) \Sigma (k_g^W)_j (k_v^C)_j}{(n-1)\ \Sigma (k_g^W)_j^2} \right]^{\frac{1}{2}} \tag{7.29}$$

and

$$\left(\frac{\hat{k}_v^C}{k_g^W}\right) - CL < \frac{k_v^C}{k_g^W} < \left(\frac{\hat{k}_v^C}{k_g^W}\right) + CL \tag{7.30}$$

7.6.4 Procedure for Intermediate Volatility Compounds

The measurements described in Section 7.6.3 should be performed as a first step in the test for intermediate volatility compounds. In this case, both terms of the two-film theory expression of k_v^C must be used (see Section 7.7.2). Estimates of k_ℓ^C and k_g^C are required to calculate k_v^C .

$$k_v^C = \frac{1}{L}\left[\frac{1}{k_\ell^C} + \frac{RT}{H_c k_g^C}\right]^{-1} \tag{7.31}$$

where R is 62.4ℓ torr K^{-1} mol^{-1}. The approximations

$$k_\ell^C \approx (D_\ell^C/D_\ell^O)^{0.7}\ (k_\ell^O) \tag{7.32}$$

and

$$k_g^C \approx (D_g^C/D_g^W)^{0.7}\ (k_g^W) \tag{7.33}$$

where D_ℓ^C and D_ℓ^O are the liquid phase diffusion coefficients of chemical and oxygen, respectively, and D_g^C and D_g^W are the gas phase diffusion coefficients of chemical and water, respectively. Experimental values of D_ℓ^O and D^W are $D_\ell^O = 2.41 \times 10^{-5}$ cm^2 sec^{-1} (at 298 K) and $D_g^W = 0.288$ cm^2 sec^{-1} (at 313 K). The value of k_ℓ^O can be calculated from measurements of k_v^O, since

$$k_v^O = \frac{1}{L}\,k_\ell^O \tag{7.34}$$

Then, for the j^{th} measurement of k_v^C,

$$k_{vj}^C = \frac{1}{L}\left[\frac{1}{(D_\ell^C/D_\ell^O)^{0.7}\ k_{\ell j}^O} + \frac{RT_j}{H_c\ (D_g^C/D_g^W)^{0.7}\ k_{gj}^W}\right]^{-1} \tag{7.35}$$

Solution of equation (7.35) for several measurements of k_{vj}^C, $k^O{}_j$, and k_{gj}^W would require iterative techniques. Since the procedure is speculative, we have not attempted the solution at this time. Experimental verification of the procedures for intermediate and low volatility compounds is clearly required.

7.6.5 Estimation of Environment Rates of Volatilization

The value of $(k_v^C)_{env}$ for high volatility compounds is estimated from equation

$$(k_v^C)_{env} = (k_v^C/k_v^O)_{lab}\,(k_v^O)_{env} \tag{7.1}$$

Representative values of $(k_v^O)_{env}$ are summarized in Table 7.2.

TABLE 7.2 OXYGEN REAERATION RATES IN REPRESENTATIVE WATER BODIES

	Literature values (day^{-1})	Suggested values[a] (day^{-1})	(hr^{-1})
Pond	0.11 - 0.23[b]	0.19	0.008
River	0.2,[c] 0.1 - 9.3[d]	0.96	0.04
Lake	0.10 - 0.30[b]	0.24	0.01

[a] Smith et al. (1977).

[b] Metcalf and Eddy (1972).

[c] Grenney et al. (1976).

[d] Langbein and Durum (1967); taken from Table 2 for rivers such as the Allegheny, Kansas, Rio Grande, Tennessee, and Wabash. Values for other rivers as well as a method for calculating k_v^O in rivers are given in this reference.

Equation (7.2) is used to estimate $(k_v^C)_{env}$ for low volatility compounds for a representative water body. In this case, there are literature reports of measurements of k_g^W only for lakes. A reasonable value for $(k_g^W)_{env}$ is 2100 cm hr^{-1} (see Section 7.7).

$$(k_v^C)_{env} = \left(\frac{k_v^C}{k_g^W}\right)_{lab} \frac{L_{lab}}{L_{env}} (k_g^W)_{env} \tag{7.2}$$

In both cases, these numbers provide rough estimates of $(k_v^C)_{env}$. The precision of the estimate of $(k_v^C)_{env}$ depends on the precision of the estimates of $(k_v^O)_{env}$ and $(k_g^W)_{env}$. More precise estimates can be made if the hydrological and meteorological characteristics of a specific water body are known.

7.7 BACKGROUND

7.7.1 Equilibrium Thermodynamics of Dilute Non-Ideal Solutions

The fundamental thermodynamics of ideal and real solutions, which includes the concepts of fugacity or escaping tendency, f, activity, a, and activity coefficient, γ, are described in any elementary physical chemistry text. We assume that the reader is familiar with these terms and will follow the thermodynamic development suggested by Lewis and Randall (1961) and Prausnitz (1969).

The fugacity is the escaping tendency of a real vapor from a real liquid and approaches the vapor pressure of the substance as the pressure approaches zero. Consider the equilibrium between a pure liquid, component i, its vapor phase, and its solution in water. Then, by definition, the fugacities of component i in all three phases are equal

$$f_i^V = f_i^o = f_i^L \tag{7.36}$$

where f_i^V is the fugacity of i in the vapor phase, f_i^o is the fugacity of pure i, and f_i^L is the fugacity of i in solution.

It is well known from experimental observations that for very dilute solutions of ideal gases in ideal solutions

$$P_i = H_i X_i \tag{7.37}$$

where P_i is the vapor pressure of solute i above the solution and X_i is the mole fraction of i, H_i is a constant. Equation (7.37) is known as Henry's law. This observation is a major foundation of the volatilization theory we are developing. Deviations from ideal behavior (H_i is not a constant) are observed at higher pressures and concentrations. Equation (7.37) can be extended to dilute real solutions by recognizing that f_i^V is nearly equal to P_i.

From the definitions of the activity, a_i, and the activity coefficient, γ_i, for solute i

$$a_i = \gamma_i X_i = f_i^L / f_i^R \tag{7.38}$$

where f_i^R is the fugacity of an arbitrary reference state of component i in the liquid phase.† Then, for solute i dissolved in a solvent,

$$f_i^L = \gamma_i X_i f_i^R \tag{7.39}$$

By combining equations (7.36) and (7.39), and assuming that $P_i = f_i^V$, we obtain

$$P_i \approx f_i^V = \gamma_i X_i f_i^R \tag{7.40}$$

By comparison with equation (7.37)

$$H_i = \gamma_i \ f_i^R \tag{7.41}$$

The activity coefficient can be defined in two ways. In the sense of Raoult's law,

$$\gamma_i \rightarrow 1 \quad \text{as} \quad X_i \rightarrow 1 \tag{7.42}$$

for both the solute and solvent. Then, the reference fugacities are equal to the fugacities of the pure liquid solute and solvent.

In the sense of Henry's law, for the solute

$$\gamma_i^* = 1 \text{ as } X_i \rightarrow 0 \tag{7.43}$$

but for the solvent

$$\gamma_i = 1 \text{ as } X_i \rightarrow 1 \tag{7.44}$$

In this case, the reference fugacity is not the fugacity of the pure liquid. Prausnitz (1969) shows that for the solute

$$\frac{\gamma_i}{\gamma_i^*} = \frac{H}{f_i} \text{ (pure i)} \tag{7.45}$$

For the purposes of this development, the Raoult's law convention is more convenient, for two reasons. First, the reference fugacity is equal to the vapor pressure of the pure liquid (at low pressures). Second, the value of γ_i can be measured easily, since for a saturated solution,

$$f_i^V = \gamma_{is} \ X_{is} \ f_i^R \tag{7.46}$$

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† Equation (7.37) assumes that a_i is independent of pressure, which is usually true if the total pressure is about 1 atm or less.

where the subscript s indicates the saturated solution. Since

$$f_i^R = f_i^L = f_i^V \approx P_i^o(\text{pure liquid}) \tag{7.47}$$

Then

$$P_i^o = \gamma_{is} X_{is} P_i^o \tag{7.48}$$

and

$$\gamma_{is} = 1/X_{is} \tag{7.49}$$

Definition of the references states is required to estimate values of γ_i and to predict solubilities (see Lewis and Randall, 1961, cpt. 20). However, we are interested in estimating values of H_c only, which can be estimated without knowing f_i^R.

For gases,

$$f_i^V = \gamma_i X_{is} f_i^R \approx P_i \tag{7.50}$$

$$H_i = \gamma_i f^R = P_i/X_{is} \text{ as } X_{is} \to 0 \tag{7.51}$$

where X_{is} is the solubility of the gas in water (moles liter^{-1}) at the gas pressure P_i.

For liquids in solution at saturation

$$f_i^V = \gamma_i X_{is} f_i^R \approx P_{i\ell} \tag{7.52}$$

$$H_i = P_{i\ell}/X_{is} \tag{7.53}$$

where X_{is} is the solubility of the liquid and $P_{i\ell}$ is the vapor pressure of the pure liquid.

For solids, we consider a saturated solution in equilibrium with the solid phase. Then

$$f_i^V = \gamma_i X_{is} f_i^R \approx P_{is} \tag{7.54}$$

In this case, f_i^R is approximately the vapor pressure of the supercooled liquid i. Then

$$H_i = P_{is}/X_{is} \tag{7.55}$$

where P_{is} is the vapor pressure of the solid i and X_{is} is the solubility of solid i.

A more convenient form of equation (7.55) and (7.57) is to use the solute concentration in moles liter^{-1} (M). Then, for liquids

$$H_{ci} = P_{i\ell}/[C_i]_{sat} \tag{7.56}$$

and for solids

$$H_{ci} = P_{is}/[C_i]_{sat} \tag{7.57}$$

which are equivalent to equation (7.5)

If vapor pressure data are available for the chemical above the melting point, T_m, but the chemical is a solid at temperature T_1 = 20°C = 293 K, then, if the vapor pressure is extrapolated to T_1, the vapor pressure is that of the supercooled liquid, $P_{is\ell}$, which is the reference state for solids in equation (7.54). Prausnitz (1969, section 9.2)has shown that

$$\ln \frac{f_{is}}{f_{is\ell}} \approx \frac{\Delta H_f}{RT_1}\left(1 - \frac{T_1}{T_m}\right) \approx \ln \frac{P_{isl}}{P_{is}} \tag{7.58}$$

where ΔH_f is the heat of fusion. Then

$$P_{is} = P_{is\ell}\left[\exp \frac{\Delta H_f}{R}\left(\frac{1}{T_m} - \frac{1}{T_1}\right)\right] \tag{7.59}$$

Substitution of equation (7.59) in equation (7.57) and conversion of X_2 to $[C_i]_{sat}$, which is a units change, gives the correct expression for H . Then the Clausius-Clapeyron equation is used to extrapolate the vapor pressure, $P_{2\ell}$ for the liquid at temperature T_2, to T_1 = 20°C, or $P_{is\ell}$ and converting $P_{is\ell}$ to the vapor pressure of the solid, gives equation (7.7)

$$H_c = \frac{P_{2\ell}}{C_{sat}}\left[\exp \frac{\Delta H_v}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]\left[\exp \frac{\Delta H_f}{R}\left(\frac{1}{T_m} - \frac{1}{T_1}\right)\right] \tag{7.7}$$

where R = 1.987 cal mol^{-1} and T_1 = 293 K.

In summary, estimates of H_{ci} can be made, provided the gas solubility versus pressure curve is measured or the liquid or solid vapor pressure and solubility in water are measured. These measurements are required at either 25°C or, preferably, 20°C, and at ambient laboratory pressures.

The implicit assumptions in the calculations are that the solutions are dilute (interactions between dissolved solute molecules do not occur) and that the gases or vapors are ideal gases ($f_i^V = P_i$). The errors introduced by these assumptions are not significant for the volatilization screening tests.

7.7.2 Two-film Theory

The two-film mass transport theory is the simplest mathematical description of the evaporation process from a liquid phase to a gas phase. This theory was originally developed by Whitman (1923) and was recently applied to the problem of the evaporation rate of chemicals from water by Liss and Slater (1974), Mackay and Leinonen (1975), Smith et al. (1977), and Smith and Bomberger (1978). The results of recent studies by Smith and Bomberger (1978) suggest that the two-film theory is not a complete description of the volatilization process of organics from water. However, it is outlined here because it is conceptually useful and because the more correct theory is too complex to describe in detail in this protocol.

The basic concept is that there are three regions near the gas-liquid interfacial surface, s: these are the liquid phase boundary layer; the Knudsen region, which is one or two mean free paths in the gas phase immediately above the gas-liquid interface; and the gas phase boundary layer. These regions are schematically depicted in Figure 7.2.

The transport of a substance through a boundary layer is assumed to be by molecular diffusion, because the fluid flow is laminar. The diffusion process can be described by Fick's law in one dimension, where the flux of the substance, N (moles $cm^{-2}sec^{-1}$) is

$$N = -D\frac{\partial C}{\partial z} \qquad (7.60)$$

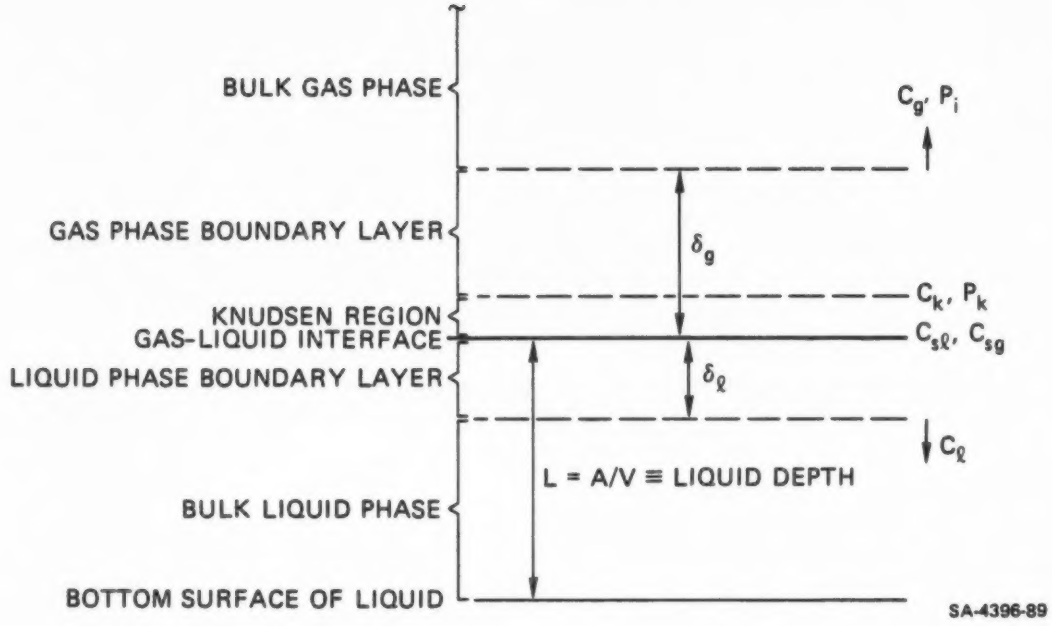
BULK GAS PHASE
GAS PHASE BOUNDARY LAYER
KNUDSEN REGION
GAS-LIQUID INTERFACE
LIQUID PHASE BOUNDARY LAYER
BULK LIQUID PHASE
BOTTOM SURFACE OF LIQUID
C_g, P_i
δ_g
C_k, P_k
$C_{s\ell}, C_{sg}$
δ_ℓ
C_ℓ
L = A/V ≡ LIQUID DEPTH
SA-4396-89

FIGURE 7.2 BOUNDARY LAYER REGIONS NEAR A GAS-LIQUID INTERFACE

where D is the diffusion coefficient and z is the vertical distance. If the concentration gradient $\partial C/\partial z$ is constant within the boundary layer, then equation (7.60) can be rewritten

$$N = k\Delta C \tag{7.61}$$

The mass transport coefficient k has the units of velocity (cm sec^{-1}) and is

$$k = D/\delta \tag{7.62}$$

where δ is the boundary layer thickness.

The flux through the gas-liquid boundary layer, $N_{s\ell}$, is

$$N_{s\ell} = k_\ell(C_\ell - C_{s\ell}) \tag{7.63}$$

where k_ℓ is the mass transport coefficient of the chemical in the liquid phase, $C_{s\ell}$ is the concentration of the chemical in the liquid phase at the gas-liquid interface. For convenience, all concentrations are expressed in units of moles cm^{-3}.

For the Knudsen region, which is just above the liquid surface and is the region where molecular velocity limits the mass transport rate, the flux, N_k, is

$$N_k = \alpha\beta(C_{sg} - C_k) \tag{7.64}$$

where

$$\beta = \left(\frac{RT}{2\pi M^c}\right)^{\frac{1}{2}} \tag{7.65}$$

where α is the accommodation coefficient, R is the gas constant (8.31×10^7 erg mol^{-1} K^{-1}), T is the absolute temperature (K), M^c is the molecular weight of the chemical, C_{sg} is the concentration of the chemical at the gas phase side of the gas-liquid interface, and C_k is the concentration of the chemical at the boundary between the Knudsen and the gas phase boundary layers (Fuchs,1959).

The flux through the gas phase boundary layer, N_g, is

$$N_g = k_g\ (C_k - C_g) \tag{7.66}$$

where k_g is the gas phase mass transport coefficient (cm sec^{-1}) and C_g is concentration of the chemical in the bulk gas phase.

For any substance, the flux through each boundary layer must be equal to the overall flux from the bulk liquid to the bulk gas phase, N. Henry's law relates C_{sg} and $C_{s\ell}$

$$C_{sg} = H\ C_{s\ell} \tag{7.67}$$

where H is the Henry's law constant (unitless, as defined here). Then, substituting equations (7.64), (7.66), and (7.67) into (7.63)

$$N = k_\ell \left[C_\ell - \frac{1}{H}\left(\frac{N}{\alpha\beta} + \frac{N}{k_g} + C_g \right) \right] \tag{7.68}$$

Collecting terms in N, and solving for N gives

$$N = \left(\frac{1}{k_\ell} + \frac{1}{\alpha\beta H} + \frac{1}{Hk_g} \right)^{-1} \left(C_\ell - \frac{C_g}{H} \right) \tag{7.69}$$

In the laboratory, $C_g \approx 0$. The volatilization rate of the chemical, R_v, is

$$R_v = \frac{A}{V} N = \frac{1}{L} N = k_v C_\ell \tag{7.70}$$

and

$$k_v = \frac{1}{L}\left(\frac{1}{k_\ell} + \frac{1}{\alpha\beta H} + \frac{1}{Hk_g} \right)^{-1} \tag{7.71}$$

For a molecule of molecular weight 150 at 20°C, $\beta = 5 \times 10^3$. For pure compounds, including water, α is between approximately 0.1 and 1.0 (Hickman, 1954; Pound, 1972). Hence, the second term of equation (7.71) is always small.* Therefore, equations (7.69) and (7.71) reduce to

$$N = \left(\frac{1}{k_\ell} + \frac{1}{Hk_g} \right)^{-1} \left(C_\ell - \frac{C_g}{H} \right) \tag{7.72}$$

$$k_v = \frac{1}{L}\left(\frac{1}{k_\ell} + \frac{1}{Hk_g} \right)^{-1} \tag{7.73}$$

Henry's law can also be written as

$$P^C = H_c\ C_W \tag{7.3}$$

---

*α may be several orders of magnitude lower if a surface active chemical is present. Then the second term may be significant.

where C_w is the concentration of the chemical in solution in moles liter^{-1} = M. The Henry's law constant, H_c, is in units of torr M^{-1}, and

$$H_c = RT\ H \qquad (7.74$$

Making the conversion to H_c and C_w(M), equations (7.72) and (7.73) become

$$N = \left(\frac{1}{k_\ell} + \frac{RT}{H_c k_g}\right)^{-1} \left(C_w - \frac{P^C}{H_c}\right) \qquad (7.75)$$

$$k_v^C = \frac{1}{L}\left(\frac{1}{k_\ell^C} + \frac{RT}{H_c k_g^C}\right)^{-1} \qquad (7.31)$$

Typical values of k_ℓ and k_g for molecules are 10-50 cm^{-1} and 1000-4000 cm hr^{-1} (Liss and Slater, 1974). The value of RT is 18,300 torr M^{-1} at 20°C. Therefore, if $H_c \sim 10^3$ torr M^{-1}. the second term in equation (7.31) is small and k_v will be determined by the value of k_ℓ. This means that the rate of mass transport (volatilization) is limited by diffusion through the liquid phase boundary layer. We have called compounds that fit within this class "high volatility compounds." Similarly, if $H_c < 10$ torr M^{-1}, then the second term in equation (7.31) dominates and the rate of volatilization is limited by mass transport in the gas phase. We have called these "low volatility compounds." If H_c is between 10 and 1000 torr M^{-1}, then both terms are important. We have called these intermediate volatility compounds."

High Volatility Compounds

For high volatility compounds, equation (7.31) becomes

$$k_v = \frac{1}{L}\, k_\ell \qquad (7.76)$$

The ratio of k_v for two high volatility chemicals, 1 and 2, is

$$\frac{k_v^1}{k_v^2} = \frac{k_\ell^1}{k_\ell^2} \qquad (7.77)$$

assuming that k_v^1 and k_v^2 are measured simultaneously. Note that (1/L) cancels.

A very convenient choice for the second chemical is oxygen ($H_c = 5.5 \times 10^4$ torr M^{-1} at 20°C, Tsivoglou, 1967). The oxygen reaeration rate is the rate at which oxygen in the atmosphere dissolves in water that has a concentration of dissolved oxygen lower than the equilibrium concentration with the atmosphere. The value of the oxygen reaeration rate constant, k_v^O, which is defined by

$$\frac{d[O_2]}{dt} = -k_v^O\left([O_2]_{sat} - [O_2]_t\right) \qquad (7.8)$$

where $[O_2]$ is the concentration of oxygen in water, $[O_2]_{sat}$ is the oxygen concentration at saturation (in equilibrium with the atmosphere), and $[O_2]_t$ is the oxygen concentration at time t. The integrated form is

$$[O_2]_t = [O_2]_{sat} - \left([O_2]_{sat} - [O_2]_o\right) e^{-k_v^O t} \tag{7.78}$$

where $[O_2]_o$ is the initial oxygen concentration. Tsivoglou has shown (Tsivoglou et al., 1965; Tsivoglou, 1967) that the ratio of the volatilization rate of several rare gases to the oxygen reaeration rate, is a constant over a wide range of turbulence conditions. Therefore, if the value of the ratio of the volatilization rate constant of a chemical, k_v^C, to the oxygen reaeration rate constant can be measured in the laboratory, then

$$(k_v^C)_{env} = (k_v^C/k_v^O)_{lab}\ (k_v^O)_{env} \tag{7.1}$$

Hill et al. (1976) used this procedure to estimate the volatilization rate of vinyl chloride in the environment. Smith et al. (1977) and Smith and Bomberger (1978) have extended this procedure to a wider range of compounds. The literature data for the ratio $k_v^C/k^O{}_v$ for high volatility compounds are summarized in Table 7.3. The available experimental results suggest that the ratio k_v^C/k_v^O is a constant over a range of k_v^O from 0.2 to 15 hr^{-1}.

In dilute solutions when the amount of material being transferred across the interface is small, the mass transfer coefficients for both gas and liquid phase mass transport can be approximated by

$$k_\ell = D_\ell/\delta_\ell \tag{7.79}$$

$$k_g = D_g/\delta_g \tag{7.80}$$

where D is the diffusion coefficient ($cm^2 hr^{-1}$) and δ is the thickness of the mass transfer film or boundary layer in the liquid or gas phase. Increasing the turbulence decreases δ and therefore increases the mass transport rate. Then, by combining equations (7.77) and (7.79) for the chemical and oxygen, we obtain

$$\frac{k_v^C}{k_v^O} = \frac{k_\ell^C}{k_\ell^O} = \frac{D_\ell^C}{D_\ell^O} \tag{7.81}$$

The validity of this equation and techniques for estimating D_ℓ^C are discussed in Sections 7.7.4 and 7.7.6.

TABLE 7.3 COMPARISON OF PREDICTED AND MEASURED VALUES OF k_v^C/k_v^O

Compounds	D_ℓ^C/D_ℓ^O [a]	$(D_\ell^C/D_\ell^O)^{1/2}$ [a]	Measured k_v^C/k_v^O	Range of k_v^O (hr-1)
Benzene	0.45	0.67	0.57 ± 0.02[b]	0.4 - 15.5
Carbon dioxide	0.84	0.92	0.89 ± 0.03[c]	0.07 - 0.5
Carbon tetrachloride	0.43	0.66	0.63 ± 0.07[b]	0.4 - 10.7
Chloroform	0.47	0.68	0.57 ± 0.05[b]	0.4 - 10.7
1,1-Dichloroethane	0.47	0.68	0.71 ± 0.11[b]	0.3 - 12.0
Dicyclopentadiene	0.31	0.56	0.54 ± 0.02[b]	1.6 - 10.4
Ethylene	0.70	0.84	0.87 ± 0.02[d]	0.1 - 2.2
Krypton	0.78[e]	0.88[e]	0.82 ± 0.08[c,f]	0.06 - 2.9
Propane	0.53	0.73	0.72 ± 0.01[d]	0.2 - 1.6
Radon	0.66[e]	0.81[e]	0.70 ± 0.08[c,f]	0.08 - 0.5
Tetrachloroethylene	0.40	0.64	0.52 ± 0.09[b]	1.6 - 10.7
Trichloroethylene	0.44	0.66	0.57 ± 0.15[b]	1.6 - 10.7

[a] D^C/D^O predicted as $(V_b^O/V_b^C)^{0.6}$, which is the result of the Othmer-Thakar approximation (Reid and Sherwood, 1966, p. 550). V_b was estimated from critical properties or the method of LeBas (Reid and Sherwood, 1966, p.86-87. $V_b^O = 25.6$ cm^3 g^{-1} mole^{-1}.

[b] SRI unpublished data.

[c] Tsivoglou, 1967.

[d] Rathbun, 1978.

[e] V_b^C from Handbook of Chemistry and Physics.

[f] Tsivoglou, 1965.

Low Volatility Compounds

For low volatility compounds, only the second term in equation (7.31) is significant. Then

$$k_v = \frac{H_c k_g}{LRT} \qquad (7.82)$$

Combining equations (7.80) and (7.82) gives

$$\frac{k_v^1}{k_v^2} = \frac{H_c^1 k_g^1}{H_c^2 k_g^2} = \frac{H_c^1 D_g^1}{H_c^2 D_g^2} = \text{a constant} \qquad (7.83)$$

which should be a constant and should be valid for low volatility compounds. We are not aware of any experimental verification of this expression.

If the volatilization rate is gas phase mass transport resistance limited, a useful equation would have the form of equation (7.1), where the ratio of the volatilization rate constant of the chemical to a second chemical found in the environment could be measured in the laboratory. The obvious choice of the second chemical is water. Thus, the water evaporation rate would be measured in the laboratory and used to estimate $(k_v^C)_{env}$ using the environmental rate for water evaporation. This concept is complicated by the fact that the rate of water evaporation is, for dilute solutions, a zero order process, since the concentration of water does not change during evaporation. Water evaporation rates are usually expressed in units of depth (length) time^{-1}, which is equivalent to units of flux, volume area^{-1} time^{-1}.

The value of k_g^W is calculated from the water evaporation rate or flux, N^W. For dilute aqueous solution, the equilibrium partial pressure of water above a solution, P_o^W, is expressed by Raoult's law (which, like Henry's law, cannot be derived from first principles.),

$$P^W = P_o^W X^W \tag{7.84}$$

where P_o^W is the vapor pressure of water at the surface temperature, and X^W is the mole fraction of water, which approximately equals 1 for very dilute solutions. Then

$$C_{sg}^W = \frac{P_s^W}{RT} \approx \frac{P_o^W}{RT} \tag{7.85}$$

Also, for water $C_\ell = C_{s\ell}$; hence, mass transport of water is only gas phase limited. Then

$$N_W = \alpha\beta \left[C_{sg}^W - \left(\frac{N_W}{k_g^W} + C_g^W \right) \right] \tag{7.86}$$

If the terms are separated,

$$N_W = \left(1 + \frac{\alpha\beta}{k_g^W} \right)^{-1} \alpha\beta \, (C_{sg}^W - C_g^W) \tag{7.87}$$

$$= \left[\frac{1}{\alpha\beta} + \frac{1}{k_g^W} \right]^{-1} \left(\frac{P_o^W - P^W}{RT} \right) \tag{7.88}$$

where P^W is the actual pressure of water vapor in the air. Since $\alpha \approx 1$ for water (Hickman, 1954), term $1/\alpha\beta$ is

$$\frac{1}{\alpha\beta} = \left[(1) \left(\frac{(8.31 \times 10^7)(293)}{2\pi(18)} \right)^{\frac{1}{2}} \right]^{-1} = 6.8 \times 10^{-5} \text{ sec cm}^{-1} \tag{7.89}$$

which is small compared to $1/k_g^W \approx 3.3 \times 10^{-4}$ cm hr^{-1} (Liss and Slater, 1974)* Therefore, equation (7.88) can be rewritten

$$k_g^W = N_W\ RT/(P_o^W - P^W). \qquad (7.90)$$

To derive the expression for (k_v^C) for low volatility compounds, it must be assumed that the ratio k_g^C/k_g^W is a constant for a wide range of laboratory and environmental conditions. This assumption is reasonable, since film theory suggests that the ratio should be proportional to the ratio of the gas phase diffusion coefficients (see Section 7.7.3), but it has not been validated by laboratory experiments. Therefore, from equation (7.85)

$$\left(\frac{k_g^C}{k_g^W}\right)_{env} = \left(\frac{k_g^C}{k_g^W}\right)_{lab} \qquad (7.91)$$

From equation (7.82)

$$k_g = k_v\ L\ RT/H_c \qquad (7.92)$$

Substitution of equation (7.92) into equation (7.91) for k_g^C in the laboratory and the environment gives

$$\frac{(k_v^C)_{env}\ RT_{env}\ L_{env}/H_c}{(k_g^W)_{env}} = \frac{(k_v^C)_{lab}\ RT_{lab}\ L_{lab}/H_c}{(k_g^W)_{lab}} \qquad (7.93)$$

and

$$(k_v^C)_{env} = \left(\frac{k_v^C}{k_g^W}\right)_{lab} \frac{L_{lab}}{L_{env}} \quad \frac{T_{lab}}{T_{env}} (k_g^W)_{env} \qquad (7.94)$$

If $T_{env} = T_{lab}$, then

$$(k_v^C)_{env} = \left(\frac{k_v^C}{k_g^W}\right)_{lab} \frac{L_{lab}}{L_{env}} \quad (k_g^W)_{env} \qquad (7.2)$$

---

*This term may be significant if a surface-active chemical is present, because α will be several orders of magnitude lower.

7.7.3 Penetration Theory

The classical two-film theory predicts that the mass transport coefficients are proportional to the diffusion coefficient (equations 7.79 and 7.80). Thus, in principle, the ratios k_v^C/k^O_v and k_g^C/k_g^W can be calculated from the ratio of the diffusion coefficients. Later theories and experimental evidence have shown that the mass transport coefficients are proportional to D^n where n may vary from 1 to ½ depending on the turbulence. These theories are described in this section.

Penetration or surface renewal theories of mass transfer across an air-water interface are based on a different model of the interface than two-film theory. Most studies, both experimental and theoretical, have focused on the liquid side of the interface; therefore, this discussion will also focus on the liquid side. The theories assume (Treybal, 1968) that instead of a fixed liquid film that sits next to the interface, packets of bulk liquid are transported to the interface, where they stay for a period of time and are then displaced by other packets from the bulk liquid. The displaced packet is mixed into the bulk liquid and loses its identity. While the packet is at the interface, material diffuses into it from the gas (or out of it, depending on the gas phase concentration). Penetration theory assumes that all of the packets reside at the interface for the same time. Surface renewal theory assumes that the residence time of packets is described by a probability distribution (Danckwerts, 1955) such that the probability of a packet being displaced is independent of its previous time history.

Both of these theories assume that the liquid packets do not reside at the interface for a time period long enough for the materials to diffuse completely through them. This is illustrated in Figure 7.3 for the case where material is being transported into the liquid. At t_o, a packet with the bulk concentration C_o arrives at the interface. At a larger time, t_1 material has started to diffuse into the packet but by time t_2, when the packet is displaced by another packet, it has not yet diffused through the packet.

The results of both theories are similar. Penetration theory yields

$$k_\ell = 2(D/\pi\theta)^{\frac{1}{2}} \tag{7.95}$$

where θ is the fixed time period that packets reside at the surface. Surface renewal theory yields

$$k_\ell = (Ds)^{\frac{1}{2}} \tag{7.96}$$

where s is the fractional rate of packet displacement. The important aspect of these two theories is that they both show that k_ℓ is proportional to the square root of the diffusion coefficient, whereas film theory shows that k_ℓ is directly proportional to the diffusion coefficient.

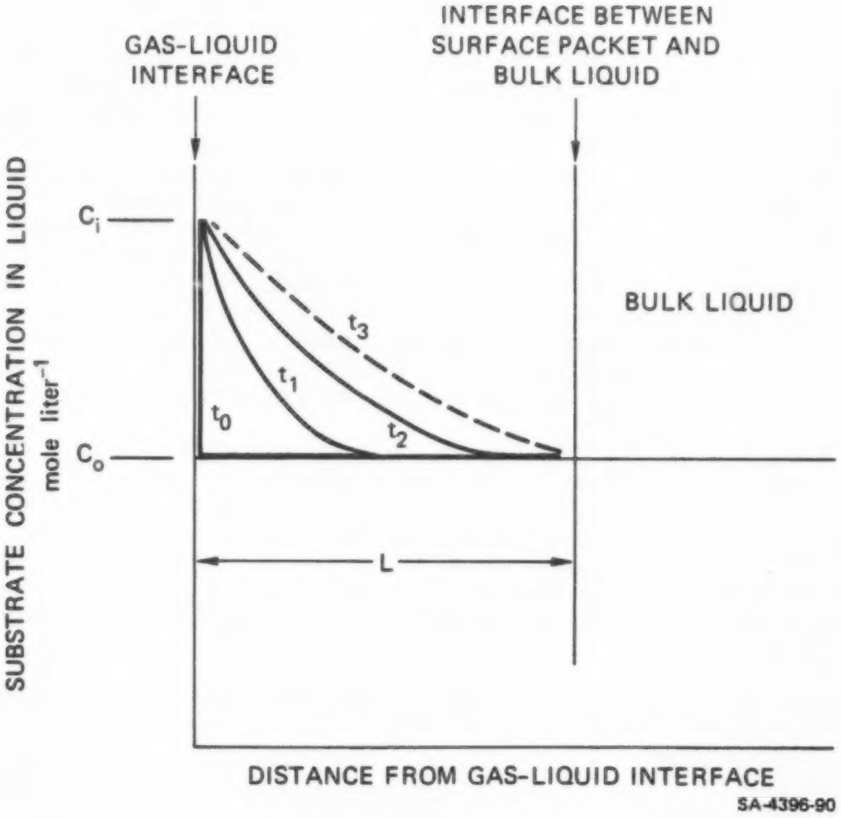

FIGURE 7.3 CONCENTRATION PROFILES USED TO DEVELOP PENETRATION AND SURFACE RENEWAL THEORIES OF MASS TRANSPORT

Dobbins (1964) proposed a modification of surface renewal theory that allows some packets to remain at the surface long enough for material to diffuse completely through the packet. This is illustrated in Figure 7.3 by the concentration profile at t_3. The consequence of this change is that k_ℓ is given by

$$k_\ell = (Ds)^{\frac{1}{2}} \coth (sL^2/D)^{\frac{1}{2}} \tag{7.97}$$

where s is again the fractional rate of packed displacement and L is the actual packet thickness. L is very similar to the film thickness parameter δ. This expression has two limiting forms: when L is small or D is large, $k_\ell = D/L$ (since $\coth (x) = 1/x$ as $x \rightarrow o$), and when L is large or D is small, $k_\ell = (Ds)^{\frac{1}{2}}$ (since $\coth (x) = 1$ as $x \rightarrow \infty$).

Therefore, in the combined theory, under different extreme circumstances either film theory or surface renewal theory obtains, and under other circumstances the dependence of k_ℓ on D is intermediate. Dobbins (1964) showed by experiments that highly agitated conditions yielded $k_\ell = D^n$ where $n \rightarrow 1/2$, meaning that surface renewal dominated mass transport. Under less agitated conditions $k_\ell = D^n$, $n \rightarrow 1$, meaning that diffusion across a film dominated mass transport. Lee (1973) used a capillary microelectrode to measure oxygen concentrations in a stirred liquid a few millimeters below the gas-liquid interface. He could detect regular concentration fluctuations, which he interpreted in terms of surface renewal theory. With this interpretation, he could estimate a value of the diffusion coefficient of oxygen in water of 2.3×10^{-6} cm^{2}sec^{-1}, which he felt compared well to a literature value of 2.2×10^{-5} cm^{2}sec^{-1}. Dobbins and Lee's work raises some questions about Tsivoglou's conjecture (1965, 1967, 1968) that the ratio of mass transport rates of gases into lakes and streams is the same as the ratio of their diffusion coefficients, namely

$$\frac{k_\ell^C}{k_\ell^O} = \frac{D^C}{D^O} = \text{constant} \tag{7.98}$$

The true relationship is probably

$$\frac{k_\ell^C}{k_\ell^O} = \left(\frac{D^C}{D^O}\right)^n = \text{constant}, \; 0.5 \leq n \leq 1.0 \tag{7.99}$$

reflecting a combination of film and surface renewal theory. Therefore, it is common to speak of a two-resistance theory, since the resistance to volatilization is the sum of resistances in the gas and liquid phases.

7.7.4 Summary of Experimental Results

Table 7.3 summarizes the measured and predicted values of k_ℓ^C/k_ℓ^O for a number of gases and organic compounds. Predictions of k_ℓ^C/k_ℓ^O have been made using molar volumes at the normal boiling point to estimate diffusion coefficients. This procedure is described in Section 7.7.5. Estimates were made for film theory and penetration theory. It is apparent that the measured value of k_ℓ^C/k_ℓ^O is consistent with $k_\ell^C/k_\ell^O = (D^C/D^O)^n$ where n is a value somewhere between 1 and 1/2. Only for one compound, ethylene, does the measured value fall outside the predicted range and even then, the error is minor.

For a number of compounds in Table 7.3, including the gases, benzene, propane and ethylene, actual values of diffusion coefficients have been measured but these values have not been used in calculating ratios. Estimated diffusion coefficients were used in all cases for two principle reasons: first, in cases where one diffusion coefficient was known and the other had to be estimated, it was felt that forming a mixed ratio might bias the results. Second, in cases where both diffusion coefficients had been measured, there was still a large potential error. Rathbun (1978) pointed out the difficulty of using diffusion coefficients measured by different investigators to calculate k_v^C/k_v^O. He calculated a k_ℓ^C/k_ℓ^O ratio for ethylene using film theory (n=1) and diffusion coefficients for oxygen and ethylene measured by the same investigator. The ratio was 0.77. If oxygen diffusion coefficients and ethylene diffusion coefficients from different investigators were used, the ratio varied from 0.57 to 0.96. This is a wider range than the range predicted by using the estimated values of the diffusion coefficients and varying n from 1 (film theory) to 0.5 (penetration theory).

In predicting $(k_v^C)_{env}$ from $(k_v^C/k_v^O)_{lab}$ ratios, there are two potential sources of error. First, conditions of mixing and flow in the natural environment (streams, ponds and lakes) will probably be different from conditions in the laboratory where k_v^C/k_v^O was measured. Under laboratory conditions n may be close to 1/2 because the turbulence is relatively high, whereas in the environment, where the turbulence is lower, n may be closer to 1 in value. Some error then results in the prediction of k_ℓ^C or k_v^C under environmental conditions. Second, if laboratory experiments are not conducted, but instead k_ℓ^C/k_ℓ^O is estimated using diffusion coefficients, the same kind of error can occur if the wrong value of n is used. The error can be on the order of ± 30% if the compound of interest is similar to those shown in Table 7.3 where $k_v^C/k_v^O \approx 0.6$.

When $H_c < 1$ torr M^{-1} (low volatility class), volatilization is controlled by mass transport in the gas phase. Mass transfer in the gas phase has been modeled by film theory, penetration theory, and surface renewal theory. Some recent work by Tamir (1978) has demonstrated for the gas phase what Dobbins demonstrated for liquid phase--namely, that a combination theory is probably required. For a series of gases, Tamir found that k_g is proportional to D^n, where n varied between 0.7 and 0.9 depending on the turbulence level. At high turbulence levels n was 0.7 and at low turbulence it was 0.9. It is expected that a wider range of turbulence conditions than those used by

Tamir would show $1/2 \leq n \leq 1$. Again, the possible difference between laboratory and environmental turbulence levels could introduce error in the predicted values.

For the protocol, we have assumed an n value of 0.7 as a compromise, because the data in Table 7.3 indicate that the error introduced for liquid phase transport control is not severe. Therefore, equation (7.91) should be rewritten as

$$\left(\frac{k_g^C}{k_g^W}\right)_{env} = \left(\frac{k_g^C}{k_g^W}\right)_{lab} = \text{constant} = \left(\frac{D_g^C}{D_g^W}\right)^{0.7} \tag{7.100}$$

Any prediction error introduced by choosing n as 0.7 would not change the fate assessment for the compound. Similarly using estimated diffusion coefficients instead of laboratory measurements probably would not change the fate assessment.

7.7.5 Estimation of Diffusion Coefficients

There are numerous ways to estimate or measure diffusion coefficients. In volatilization theory where ratios of diffusion coefficients are required, most investigators have used Tsivoglou's suggestion (1965, 1967, 1968) for diffusion in water and have estimated D^1/D^2 as d^2/d^1 where d is the molecular diameter of the compound being considered. For cases where gas phase diffusion is important, investigators have followed Liss' suggestion (Liss and Slater, 1974) and estimated D^1/D^2 as $(M^2/M^1)^{1/2}$ where M is the molecular weight of the compound.

Neither of these approaches is correct. Reid and Sherwood (1966) have thoroughly reviewed the literature on predicting diffusion coefficients using other physical properties of materials. They observe, for example, that diffusion coefficients in solution are inversely proportional to molecular diameter only for large spherical molecules. Gas molecules and most organics of concern are too small for the approximation to be correct. It is true, however, that for most compounds the estimates of the ratio of mass transport coefficients based on molecular weight or molecular diameters are within a factor of 2 or 3 from the correct result.

Diffusion in Liquids

Most methods for estimating diffusion coefficients in solution use the solute molar volume at its normal boiling point. When the solvent is water, the Othmer-Thakar relation is the most convenient (Reid and Sherwood, 1966, p.550)

$$D^C\ (\text{cm}^2/\text{sec}) = \frac{14.0 \times 10^{-5}}{\mu_w^{1.1}\ V_b^{0.6}} \tag{7.101}$$

where μ_w is the viscosity of water (centipoise) at the temperature of concern, and V_b is the molar volume ($\text{cm}^3 \text{g}^{-1}\text{mol}^{-1}$) at its normal boiling point of the solute C. This relation has beem compared to measured diffusion coefficients and found to be accurate within ± 11%. When the molar volume is not known, it can be estimated from the critical pressure (Reid and Sherwood, 1966, p.87) or assembled from molar volume increments proposed by LeBas (Reid and Sherwood, 1966, p. 86). Then, k_ℓ^C/k_ℓ^0 can be estimated from equations (7.99) where n = 0.7 and (7.101)

$$\frac{k_\ell^C}{k_\ell^0} = \left(\frac{D_\ell^C}{D_\ell^0}\right)^{0.7} = \left[\left(\frac{V_b^0}{V_b^C}\right)^{0.6}\right]^{0.7} = \left(\frac{V_b^0}{V_b^C}\right)^{0.42} \qquad (7.102)$$

For the light gases, molar volumes have been estimated using equation (7.101) and diffusion coefficient measurements. When critical pressure measurements are absent, critical pressure can be estimated by the increment method of Lydersen (Reid and Sherwood, 1966, p.9). Critical pressure estimation errors are typically ±3% as are the molar volume estimates. This means that diffusion coefficient estimates in water should be accurate within ±15%.

Diffusion in Gases

There are several rather complex methods for estimating diffusion coefficients in gases based on statistical mechanics. All the methods require knowledge of the Lennard-Jones parameters σ and ε for the diffusing species and the stationary phase. For many compounds these parameters would have to be estimated, which in turn would require information on critical pressure and volume. A much simpler procedure when the stationary phase is air is to use (Reid and Sherwood, 1966, p. 531)

$$D^C(\mathrm{cm}^2\ \mathrm{sec}^{-1}) = P \times 2.52 \times 10^7\ \mu_A^{2.74} \left\{ \frac{\left(\frac{M_A + M_C}{M_A M_C}\right)^{\frac{1}{2}}}{(V_{b,A}^{0.4} + V_{b,C}^{0.4})^2} \right\}^{1.23} \qquad (7.103)$$

where P is the pressure (atm), μ_A is the viscosity of air (centipoise) at the system temperature, V_b is the molar volume at the normal boiling point, M_A is the molecular weight of air, and M_C is the molecular weight of the compound. This correlation has an average error of ±9%.

Liss and Slater (1974) have assumed that k_g and D_g are inversely proportional to the square root of the molecular weight of the chemical. In view of the uncertainties in the estimates of H_c and D_g, this assumption may be adequate for many purposes. Thus,

$$\frac{k_g^C}{k_g^W} = \left(\frac{D_g^C}{D_g^W}\right)^{0.7} \approx \left(\frac{M^W}{M^C}\right)^{0.5} \qquad (7.104)$$

7.7.6 Calculation of Environmental Volatilization Rate Constants

High Volatility Compounds

If the volatilization rate is liquid phase mass transport resistance limited, equation (7.1) is used to estimate $(k_v^C)_{env}$. The following

$$(k_v^C)_{env} = (k_v^C/k_v^O)_{lab}\,(k_v^O)_{env} \qquad (7.1)$$

equation, which is the combination of equations (7.81) and (7.99),

$$(k_v^C/k_v^O)_{env} = (k_v^C/k_v^O)_{lab} \approx (D_\ell^C/D_\ell^O)^{0.7} \qquad (7.105)$$

Values of $(k_v^O)_{env}$ are given in Table 7.2.

Low Volatility Compounds

If the volatilization rate is gas phase mass transport limited, equation (7.2) is used to estimate $(k_g^W)_{env}$

$$(k_v^C)_{env} = \left(\frac{k_v^C}{k_g^W}\right)_{lab} \frac{L_{lab}}{L_{env}}\,(k_g^W)_{env} \qquad (7.2)$$

We believe that the ratio k_v^C/K_g^W should be constant for low volatility compounds.

The value of $(k_g^W)_{env}$ must be estimated from field data. The water evaporation rate, which is gas phase mass transport resistance limited (Liss and Slater, 1974), has been carefully measured for several lakes. The results are shown in Table 7.4.

TABLE 7.4 WATER EVAPORATION RATES FOR LAKES

Location	Average evaporation rate (cm sec^{-1} x 10^6)	Reference
Lake Hefner, Oklahoma	4.8	Marciano and Harbeck (1952)
Lake Mead	6.8	Harbeck, et al. (1958)
Pretty Lake, Indiana	3.8	Ficke (1972)
Average	5.1	

Assuming that the average relative humidity is 50%, then the average value of k_g^W for freshwater lakes is,

$$k_g^W = N_W\ RT/(P_o^W - P^W) \qquad (7.90)$$

$$= \frac{(5.1 \times 10^{-6})(62400)(293)}{(18)\ (17.5)\ (0.5)}$$

$$= 0.59\ \mathrm{cm\ sec}^{-1}$$

$$= 2100\ \mathrm{cm\ hr}^{-1}$$

Equations (7.82) and (7.104) can be used to estimate values of k_v^C/k_g^W, since

$$k_v^C = \frac{H_c\ k_g^C}{L\ RT} \qquad (7.82)$$

$$\frac{k_g^C}{k_g^W} = \text{constant} \approx \left(\frac{D_g^C}{D_g^W}\right)^{0.7} \qquad (7.100)$$

$$\frac{k_v^C\ L_{lab}}{k_g^W} = \frac{H_c\ k_g^C}{RT\ k_g^W} = \frac{H_c}{RT}\left(\frac{D_g^C}{D_g^W}\right)^{0.7} \qquad (7.105)$$

Thus, values of H_c, D_g^C, and D_g^W must be estimated or measured. Then the value of $k_v^C/(A/V)_{lab}\ k_g^W$ can be substituted in equation (7.2) to give an estimate of $(k_v^C)_{env}$. Liss and Slater (1974) suggested that

$$\frac{k_g^C}{k_g^W} = \left(\frac{M^C}{M^W}\right)^{\frac{1}{2}} \qquad (7.106)$$

Using this approximation,

$$\frac{k_V^C \cdot L_{lab}}{k_g^W} = \frac{H_c}{RT}\left(\frac{M^C}{M^W}\right)^{\frac{1}{2}} \qquad (7.107)$$

These equations have not been verified in the laboratory.

Then, substituting equation (7.105) or (7.107) into equation (7.2), we obtain

$$(k_v^C)_{env} = \left(\frac{k_v^C}{k_g^W}\right)_{lab} \frac{(A/V)_{env}}{(A/V)_{lab}} (k_g^W)_{env} \qquad (7.2)$$

$$= \frac{H_c}{RT}\left(\frac{D_g^C}{D_g^W}\right)^{0.7} \frac{1}{L_{env}} \quad (k_g^W)_{env} \qquad (7.108)$$

$$\approx \frac{H_c}{RT}\left(\frac{M^W}{M^C}\right)^{0.5} \frac{1}{L_{env}} \quad (k_g^W)_{env} \qquad (7.109)$$

The following procedure was used to estimate the lower limit of H_c that would cause the environmental half-life for volatilization of a low volatility compound to be less than 3 months. The half-life for volatilization of the chemical, $t_{1/2}$, can be calculated from

$$t_{1/2} = \ln 2/(k_v^C)_{env} \qquad (7.106)$$

If the half-life is less than 3 months, then $\left(k_v^C\right)_{env}$ must be greater than 9×10^{-8} sec^{-1}.

Substituting the following representative values into equation (7.109), and solving for H_c, we obtain

$$(k_v^C)_{env} > 9 \times 10^{-8} \text{ sec}$$

$$M^C = 250$$

$$R = 62{,}400 \text{ torr cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$$

$$L_{env} = 200 \text{ cm}$$

$$T = 20^oC = 293 \text{ K}$$

$$(k_g^W)_{env} = 2100 \text{ cm hr}^{-1} = 0.59 \text{ cm sec}^{-1}$$

$$H_c > \frac{(9 \times 10^{-8})(62.4)(293)(200)}{(18/250)^{\frac{1}{2}}\ (0.59)}$$

$$> 2.1 \text{ torr M}^{-1}$$

Thus, if H_c is greater than about 2 torr M^{-1}, the environmental volatilization half-life of the chemical may be less than 3 months.

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CHAPTER 8. SORPTION OF ORGANICS ON SEDIMENTS

by

J. H. Smith and D. C. Bomberger

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8. SORPTION OF ORGANICS ON SEDIMENTS

8.1 INTRODUCTION

Sorption of organic substrates into sediments and biota can be a very important phenomenon in the aquatic environment. The sediments can act as sinks for sorbed materials, removing them from the water column. However, since the substrate can also be released (desorbed) from the sediments at a later time, contaminated sediments can also be a source of pollution. Sorption of pollutants by sediments often results in high concentrations of low-solubility pollutants in a part of the water column where uptake by biomagnification may become significant.

The use of the terms "sorption" and "adsorption" deserves special comment. Sorption includes any type of process whereby the substrate is physically or chemically bound to a solid surface (chemisorption). Adsorption implies to us that the process that holds the substrate on the sediment is strictly physical, such as the van der Waals type of attraction. However, sorption of ionizable substrates such as amines may include chemical bonding interactions as well as physical processes. While other authors have used adsorption to include chemical interactions (Hamaker and Thompson, 1972), we will use "sorption" to avoid confusion.

These protocols are designed to provide necessary information on the extent of sorption of organic and organometallic compounds on naturally occurring sediments. The procedures can also be used to measure the sorption isotherm on soils.

8.2 SUMMARY

Screening and detailed test protocols for sorption of chemicals on sediments have been prepared to enable the investigator to estimate the equilibrium sorption partition coefficient of a chemical on suspended or bottom sediments in natural waters. Only chemicals with a sorption partition coefficient greater than 100 are considered for detailed studies.

The test protocols are based on a review of the extensive body of literature on sorption and an analysis of the kinetics and equilibria of the sorption process. The recommended test protocols meet the criteria of quantitation, accuracy, and applicability to experimental systems. They are cost effective and are simple to use for a wide range of chemical structures.

The sorption partition coefficient, K_p, is defined as

$$K_p = \frac{\text{concentration of chemical sorbed on sediment } (\mu g\ g^{-1})}{\text{concentration of chemical dissolved in water } (\mu g\ ml^{-1})} \tag{8.1}$$

$$= F_{oc}\ K_{oc}$$

where F_{oc} is the fraction organic content and K_{oc} is the sorption partition coefficient normalized for the sediment organic content. The screening protocol consists of estimating K_{oc} from the solubility of the chemical in water and measuring K_p and K_{oc} at one concentration of chemical and two sediment loadings, using a standard sediment. If the value of K_p is greater than 100, the detailed test protocol should be used.

The detailed protocol consists of the experimental plan for measuring the partitioning between sediment and water at several sediment concentrations and total concentrations of the chemical. A nonlinear least squares procedure is used for calculating the best estimate of K_p.

8.3 CONCLUSIONS

Present knowledge of the theory and experimental aspects of the sorption of chemicals on soils and sediments provides a sound basis on which to propose protocols for evaluating the extent of sorption in natural waters. The recommended sorption protocols represent a balance between the economic need to minimize laboratory work and the scientific requirements for sufficient and accurate data.

The general protocol has been evaluated under laboratory conditions (Smith et al., 1978). Measurements of the sorption partition coefficient on the sediment of specific water bodies that may be exposed to the chemical are recommended.

8.4 RECOMMENDATIONS

The basic protocol has been evaluated (Smith et al., 1978) using a limited range of sediments. We recommend that a series of test soils and sediments spanning a reasonable range of cation exchange capacity and total organic carbon be selected, stored, and maintained in large enough quantities so that samples can be made available to researchers.

8.5 SELECTION AND PREPARATION OF SEDIMENT SAMPLES

At the time of preparation of this protocol, no reference soil or sediment samples are available for standardized measurement of sorption isotherms. Therefore, we recommend that the user collect approximately six freshwater sediments from a variety of sources, including, if appropriate, a sample from a proposed receiving water body. Natural sediments change on a daily basis, due to chemical and biological transformations of the organic matter, sediment transport within the water column, and changes in the hydrological properties of the water body that occur on a seasonal basis. They also vary as a function of the depth and location. Therefore, enough of each sediment should be collected to permit all the experimental work to be performed on a given sample. It would be nearly impossible to obtain a duplicate sample later.

The sediments should be chosen to uniformly span the range of organic content (OC), cation exchange capacity (CEC), and pH commonly found for sediments and soils. Sediments should be obtained from streams, rivers, eutrophic lakes, and oligotrophic lakes. Special care should be taken to follow uniform and consistent methods of sampling, preservation, and transport of sediments. At the time of sampling, detailed records should be made of the exact sampling locale and the representativeness of the sample collected in relation to the size of the water body, depth from water surface, local topography, and any special feature peculiar to that area.

The chemical and physical characteristics of a natural sediment depend on the type of soil upstream from a given location because soil runoff forms the sediment. Data regarding the surrounding soils can be obtained from the local soil survey, hydrologic/geological survey, water resources board, and public health departments to help select sediments that cover the required range of OC, CEC, pH, and clay mineral compositions. Information from these sources will cover the parent material, soil physical and chemical properties, and clay mineral composition. Background soil survey data of the land from which the sediment orginated, such as the crop, fertilizer, and insecticide/herbicide history of that land, and the rate of sedimentation and the microbial life of the water body should be obtained, if available.

The collected sediments should be analyzed for pH, cation exchange capacity, organic carbon, and size distribution, using the methods outlined and referenced below.

8.5.1 pH

Measurement of the pH of a sediment is important when working with compounds whose ionization state is affected by pH. The strength of sorption will depend on the degree of ionization, particularly where the sorption mechanism is ion exchange.

The pH of the sediments should be measured by the method described by Peech (1965). Two parts of a solution of 0.01 M $CaCl_2$ are added to one part of a sediment to adjust the ionic strength of the suspension. The suspension is stirred several times during the next 30 minutes. The suspension is left to settle for 30 minutes and the pH of the supernatant is measured with a glass pH electrode containing an internal calomel reference electrode.

8.5.2 Cation Exchange Capacity (CEC)

An important parameter of the sediment when dealing with ionizable compounds is CEC. The degree of sorption of the compound by the sediment can be directly related to the CEC of the sediment. The method used consists of saturating the sediment with NH_4^+, washing away excess NH_4^+, distilling NH_3 into dilute H_2SO_4. This method is based on one developed by Mackenzie (1951).

8.5.3 Organic Carbon

The organic matter of sediments is a major source of sorption of nonionized compounds on sediments. The amount of organic matter can be determined by an organic carbon (OC) analysis. This value can be correlated with the degree of sorption by different sediments. The analytical methods for organic carbon are not specific and yield varying results depending on the method used. However, the trend between sediments should be in the same direction.

One method is that of Walkley and Black (Hesse, 1971). The organic carbon is oxidized by a wet dichromate digestion, and the excess dichromate is titrated with ferrous ion in the presence of barium diphenylamine sulfonate. The organic carbon obtained from the analysis is multiplied by a correction factor of 1.33.

The second method is a dry combustion technique (Hesse, 1972). The dried sediment sample is placed in a combustion tube through which oxygen is passed, and the tube is heated to 1000°C. The evolved CO_2 is collected and weighed. To rid this analysis of interferences by carbonate, the sediment is first acidified before drying. Several commercial laboratories routinely make this measurement.

8.5.4 Size Distribution

The size distribution of the sediment is determined using ASTM Methods D421 and D422-63 (ASTM, 1978). The sample is prepared according to ASTM Method D421. The size distribution of the fraction of the dry sediment that is retained on the No. 10 (2.00-mm) sieve is determined by further sieving and then by sedimentation, using ASTM Method D422-63. The weight percent of the size fractions shown in Table 8.1 should be reported for each test sediment, using the format suggested in this table.

Table 8.1. SEDIMENT SIZE FRACTIONS

Fraction	Retained on sieve	Size Range[a] (cm)	Time to settle 10 cm (sec)	Time to settle 10 cm (min)
Gravel	No. 4 (4.8 mm)	$> 4.8 \times 10^{-1}$	-	-
Coarse sand	No. 10 (2.0 mm)	4.8×10^{-1}-2×10^{-1}	0.03	-
Medium sand	No. 40 (425 μm)	2×10^{-1}-4.2×10^{-2}	0.63	-
Fine sand	No. 200 (75 μm)	4.2×10^{-2}-7.5×10^{-3}	19.8	-
Coarse silt	-	7.5×10^{-3}-2×10^{-3}	278	4.6
Medium silt	-	2×10^{-3}-5×10^{-4}	4450	74.2
Fine silt	-	5×10^{-4}-2×10^{-4}	2.8×10^4	464
Clay	-	$< 2 \times 10^{-4}$	-	-

[a] Particle diameter. The size of the silt and clay fractions are the equivalent Stokes diameters for spheres.

8.5.5 Preparation of the Sediment

Each sediment sample should be sieved wet through a No. 10 (2.0-mm) sieve to remove the large organic debris, rocks, and gravel. It should then be quartered and stored in small polyethylene jars at 4°C.

It is very difficult to make reproducible transfers of whole sediments if the sediments are in suspension. The sand fractions settle rapidly, and they constitute a significant portion of the total mass of many sediments. Therefore, only the particles smaller than 60 μm (6×10^{-3}cm) should be used. The less than 60-μm sediment fraction (silt and clay) can be reproducibly transferred as a slurry. Also, the majority of the sorption occurs on these fractions and not on the sand and gravel fractions. The less than 60-μm sediment is prepared by adding the wet sediment to a 2-liter bottle, mixing it thoroughly by shaking for several minutes, and settling the screened sediment for 30 seconds to remove the sand and gravel. The discarded fractions are dried and weighed. The calculations will assume that the discarded fractions contribute mass to the sediment, but not to sorption.

To determine the concentration of sediment in the suspension, C_{ss}, the sediment is resuspended by shaking for 1 minute. The suspension is allowed to settle for 30 seconds, and the suspended portion is drawn off into another container using a syphon. A 10-ml aliquot of this suspension is added to an aluminum weighing dish using a 10-ml measuring pipet with a large tip opening. The suspension is constantly stirred during this process with a magnetic stirrer to ensure the homogeneity of the suspension. The dish is placed in a drying oven at 110°C and then weighed to constant weight after the sediment is completely dry. Three determinations are made and the mean taken as the value of C_{ss}.

8.6 SCREENING TESTS

8.6.1 Purpose

This screening test protocol is intended to identify chemicals with sorption partition coefficients K_p greater than 100.

8.6.2 Procedure

It is essential to measure the solubility of the chemical in distilled water before beginning the sorption test protocol. If solid (or liquid) phase pure chemical remains suspended in the aqueous phase, erroneous values of the sorption partition coefficient will be obtained.

The sorption partition data will be fit to a Freundlich isotherm with an exponent of 1.

$$C_s = K_p C_w = (K_{oc} F_{oc})C_w \qquad (8.2)$$

where

$$K_p = K_{oc} F_{oc} \qquad (8.3)$$

and

C_s = concentration of chemical on the sediment at equilibrium (μg g^{-1} sediment)

K_p = sorption partition coefficient

K_{oc} = sorption partition coefficient normalized by the organic content

F_{oc} = fraction organic content (weight basis)

C_w = concentration of chemical in the water at equilibrium (μg ml^{-1} = mg $liter^{-1}$).

Estimation of K_{oc}

An estimated value of K_{oc}, which is called K_{oc}^{est}, is used to calculate the concentrations of chemical and sediment for the screening isotherm. Express the solubility of the chemical in distilled water, C_{sol}, in moles $liter^{-1}$ (M). Equation (8.4), which is the least squares fit to the data plotted in Figure 8.1, is used to calculate K_{oc}^{est}.

$$\log K_{oc}^{est} = -0.27 - 0.782 \log(C_{sol}) \qquad (8.4)$$

The available data suggest that K_{oc}^{est} should be within an order of magnitude of K_{oc}.

Preparation of the Stock Solution of the Chemical

A stock solution of the chemical in distilled or distilled-deionized water is used to prepare all the chemical-sediment mixtures used in the isotherm experiments. The initial concentration of the chemical in the stock solution, C_o, should be saturated or 1 mg $liter^{-1}$, whichever is lower.

Experimental Plan for the Screening Isotherm

The experimental plan for the screening isotherm is given in Table 8.2.

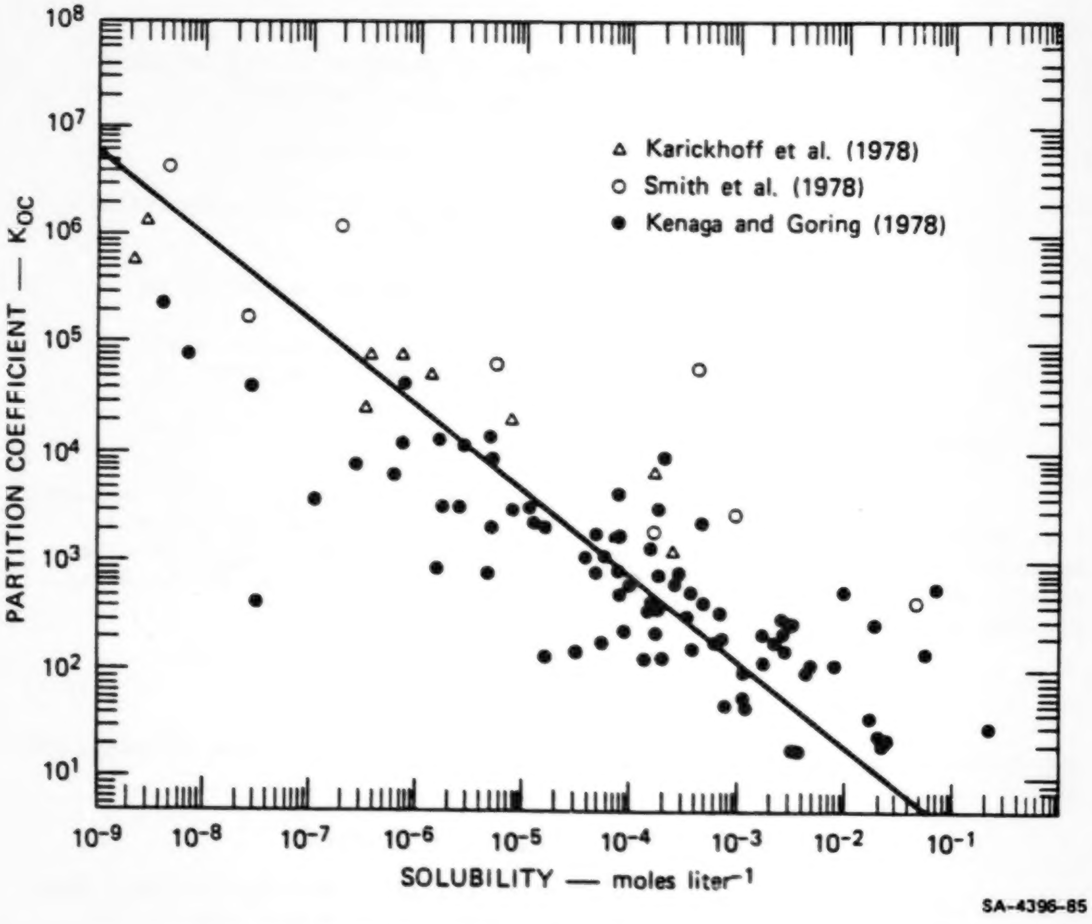

FIGURE 8.1 SOIL OR SEDIMENT PARTITION COEFFICIENT OF CHEMICALS VERSUS SOLUBILITY IN WATER

TABLE 8.2. EXPERIMENTAL PLAN FOR SCREENING SORPTION ISOTHERM MEASUREMENTS[a]

	Number of flasks		
Concentration of chemical	No sediment	Low sediment	High sediment
None	1	0	1
Low	1	2	2

[a] Replicate measurements should be made of C_w and C_s at equilibrium in each flask.

To set up the screening isotherm, the following quantities must be defined and either chosen or measured:

C_o = concentration of the chemical in the stock solution (mg liter^{-1})

V_t = total volume of suspension after adding a volume of the sediment suspension (V_s), a volume of the chemical stock solution (V_c), and the volume of makeup water (V_m) (liters). All volumes must be expressed in ml.

= $V_s + V_c + V_m$

C_{ss} = g sediment per ml of sediment stock suspension

F_s = estimated fraction of chemical sorbed

F_{oc} = fraction organic carbon of the sediment selected for the screening isotherm

V_s = volume of sediment stock solution.

The equations that describe the quantities that must be used are:

$$C_s = (K_{oc}^{est} F_{oc})\ C_w = K_p^{est}\ C_w \tag{8.5}$$

$$\frac{C_o V_c F_s}{C_{ss} V_s} = (K_{oc}^{est} F_{oc})\ \frac{C_o\ V_c\ (1 - F_s)}{V_t} \tag{8.6}$$

and, solving equation (8.6) for V_s, we obtain

$$V_s = \frac{F_s\ V_t}{(K_{oc}^{est}\ F_{oc})\ (1 - F_s)\ C_{ss}} \tag{8.7}$$

We chose $V_c = 0.5\ V_t$ for convenience. Also, to be sure that the change of the concentration of the chemical in the water can be measured reliably, the values of F_s at low and high sediment concentrations should be approximately 0.15 and 0.85, respectively. Then

$$V_c = 0.5\ V_t \tag{8.8}$$

$$V_s^l = \frac{0.15\ V_t}{(K_{oc}^{est}\ F_{oc})\ (1 - 0.15)\ C_{ss}} \quad \text{(low sediment)} \tag{8.9}$$

$$V_s^h = \frac{0.85\ V_t}{(K_{oc}^{est}\ F_{oc})\ (1 - 0.85)\ C_{ss}} \quad \text{(high sediment)} \tag{8.10}$$

$$V_m = V_t - V_s - V_c \tag{8.11}$$

where V_m is the volume of water added to make up the volume to V_t. The superscrips, l and h, are used to indicate high or low sediment or chemical concentrations.

Note that to prepare the sediment-chemical mixtures as recommended here,

$$V_s^h < V_t - V_c \tag{8.12}$$

To meet this requirement, the concentration of the sediment stock suspension must be adjusted so that

$$C_{ss} > \frac{F_s V_t}{(K_{oc}\ F_{oc})\ (1 - F_s)\ (V_s^h)} \tag{8.13}$$

The greatest amount of sorption, $F_s = 0.85$, will occur in the high sediment flask. Then,

$$C_{ss} > \frac{0.85\ V_t}{(K_{oc}\ F_{oc})\ (0.15)\ V_s^h} \tag{8.14}$$

The following values were selected for illustration.

$$V_t = 100 \text{ ml}$$

$$K_{oc}^{est} = 10^5$$

$$F_{oc} = 0.05$$

Then, since $V_s^h \leq 0.5\ V_t$

$$C_{ss} > \frac{0.85\ V_t}{(10^5)\ (0.05)(0.15)(0.5)\ V_t}$$

$$> 2.27 \times 10^{-3} \text{ g ml}^{-1}$$

If $C_{ss} = 0.004$ g ml^{-1}, then substituting in equations (8.8) through (8.11) gives

$$V_s^l = \frac{(0.15)(100)}{(10^5)\ (0.05)(0.85)(0.004)} = 0.88 \text{ ml}$$

$$V_s^h = \frac{(0.85)(100)}{(10^5)\ (0.05)(0.15)(0.004)} = 28.3 \text{ ml}$$

For convenience, $V_s^l = 1.0$ ml and $V_s^h = 30.0$ ml could be selected. If this were done, the actual fractions sorbed would be 0.167 and 0.86 in the low and high sediment flasks, respectively. This calculation was made by solving equation (8.6) for F_s and substituting the appropriate values.

$$F_s = \frac{(K_{oc}^{est}\ F_{oc})C_{ss}\ V_s}{V_t + (K_{oc}^{est}\ F_{oc})C_{ss}V_s} \qquad (8.15)$$

Also,

$$V_m = V_t - V_s - V_c \qquad (8.16)$$

and therefore

$$V_m^l = 100 - 1.0 - 50 = 49.0 \text{ ml}$$

$$V_m^h = 100 - 30.0 - 50 = 20.0 \text{ ml}$$

Measurement of the Screening Sorption Isotherm

To prepare the no chemical/no sediment blank, place V_t liters of water in a clean flask.

To prepare the low chemical/no sediment blank, add V_c liters of chemical stock solution to a flask, then add $(V_t - V_c)$ liters of distilled water.

To prepare the no chemical/high sediment blank flasks, dilute V_s^h liters of sediment stock solution* with $(V_t - V_s^h)$ liters of distilled water.

To prepare the chemical/sediment flasks, add to the flask V_c liters of chemical stock solution, V_s^l or V_s^h liters of sediment stock solution, and either $V_m^l = V_t - V_c - V_s^l$ or $V_m^h = V_t - V_v - V_s^h$ liters of distilled water.

All three blanks should be shaken, extracted, and analyzed at the same time as chemical/sediment flasks are analyzed. Replicate flasks containing chemical and sediment are required; single, blank flasks are required for the screening isotherm.

All solutions, suspensions, and blanks should be made up in clean 500-ml Erlenmeyer flasks, which are then sealed, covered with aluminum foil to exclude light, and shaken gently on a wrist-action shaker for 12 to 16 hours (that is, overnight). If shorter equilibration times are used, the sorption equilibrium may not be attained. If longer equilibration times are used, transformation processes, mainly biodegradation, may occur. In some cases, biodegradation may occur within 12 hours (Smith et al., 1978). In that case, a 2- to 4-hour equilibration time should be used.

Centrifugation Conditions

At the end of the equilibration period, the contents of each flask must be centrifuged to separate the sediment from the supernatant. The centrifugation conditions should be chosen to remove particles greater than about 0.5 µm (5×10^{-5} cm) equivalent diameter (to settle all but the fine clay fraction). There are two ways to specify the conditions: by determining the relative centrifugal force, RCF, or by calculating the centrifugation time, t_c.

The RCF is defined as

$$\mathrm{RCF} = \omega^2 R/g \tag{8.17}$$

$$= 1.117 \times 10^{-5}\, RN^2 \tag{8.18}$$

where

ω = angular velocity of the centrifuge spindle radius(sec^{-1})

R = radial distance of the particle from the center of rotation

g = gravitational constant (980.1 cm sec^{-2})

N = number of revolutions (min^{-1}).

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*One sediment is used for all screening isotherm experiments.

The value of RCF as a function of RPM and the centrifuge head is usually given in the centrifuge manual. The value of RCF x g can be used to specify the centrifugation conditions; the conditions needed to centrifuge particles greater than 0.5 μm (5×10^{-5} cm) diameter may be determined from Figure 8.2.

The centrifugation time determined from Figure 8.2 is approximate because the gravitational force exerted on a particle increases as it settles in the centrigute tube. A more accurate procedure is to use equation (8.19) to calculate the centrifugation time, t_c:

$$t_c(\text{sec}) = \frac{4\eta \ln(R_2/R_1)}{\omega^2 D^2 (\rho_p - \rho_\ell)K} = 4.04 \times 10^8 \ln (R_2/R_1)/\omega^2 \qquad (8.19)$$

where

t_c = centrifuge time

η = absolute viscosity of the liquid (poise) = 0.0100 for water

R_2 = distance from centrifuge spindle to deposition surface of centrifuge tube (cm) (see Figure 8.2)

R_1 = distance from spindle to surface of the sample (cm) (see Figure 8.2)

ω = rotational velocity (radians sec^{-1}) = $4\pi^2 N^2/3600$ where N is the revolutions per minute of the centrifuge

D = diameter of the particle (cm) = 2×10^{-5} cm

ρ_p = density of the particle (g cm^{-3}) ≈ 2.65 g cm^{-3} for sediment

ρ_ℓ = density of the liquid (g cm^{-3}) = 1 g cm^{-3} for water

K = shape factor ≈ 0.15.

This equation takes into account the increased gravitational force between R_1 and R_2. R_1 and R_2 are defined in Figure 8.3; they must be measured for each centrifuge head. Substitution of representative values in equation (8.19) yields

$$t_c(\text{min}) = 1.41 \times 10^9 \log(R_2/R_1)/N^2 \qquad (8.20)$$

After centrifuging, the aqueous phase is decanted carefully from the sediment. About one milliliter of solution will probably be retained in centrifuge tube. One extraction and replicate analyses of the chemical in the supernatant extract must be performed initially. (This necessarily requires that suitable extraction and analytical techniques must be available

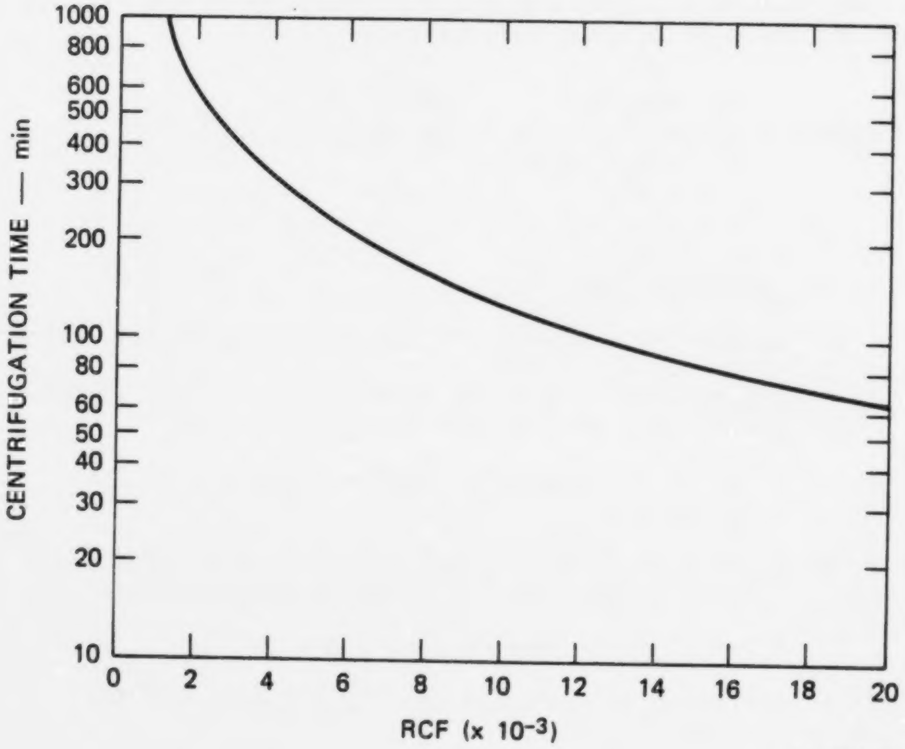
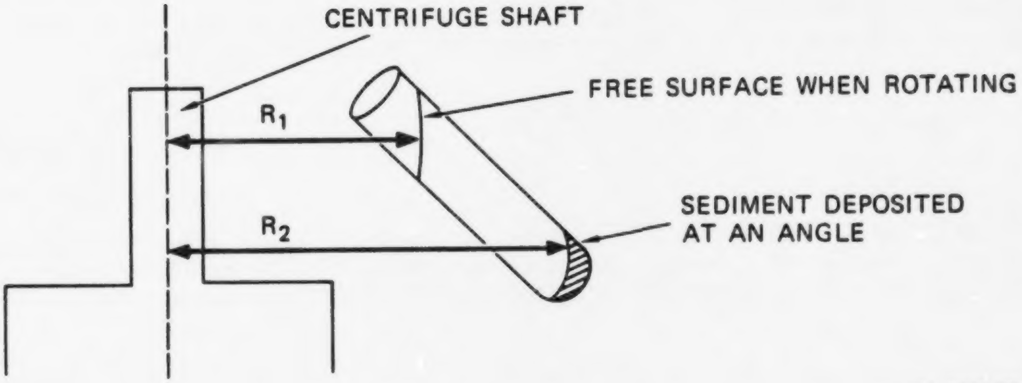


FIGURE 8.2 MINIMUM CENTRIFUGATION TIME VERSUS RCF (AT THE TUBE TIP) REQUIRED TO REMOVE 0.2-μm-DIAMETER (2×10^{-5}cm) PARTICLES


CENTRIFUGE SHAFT
FREE SURFACE WHEN ROTATING
R_1
SEDIMENT DEPOSITED AT AN ANGLE
R_2

SA-4396-87

FIGURE 8.3 DEFINITION OF RADII OF A CENTRIFUGE

for the chemical.) Standard solutions of the chemical must also be analyzed.

If the distilled water blank contains more than 5% of the amount of chemical measured in the low sediment flask, the experiments should be repeated to see if the glassware, water, or solutions were contaminated or a new analytical method must be devised (presuming that the interference is not the chemical of interest).

Data Analysis

A preliminary estimate of the partition coefficient from the screening isotherm data (K_p^{scr}) is obtained by substitution into equation (8.5), based only on the average of the measurements of C_w in one set of flasks.

$$K_{oc}^{scr} F_{oc} = K_p^{scr} = \frac{C_o V_c - \bar{C}_w V_t}{C_{ss} V_s \bar{C}_w} \tag{8.21}$$

The data for C_w from either the high or low sediment flask should be used. The actual values of V_c and V_s added to each flask should be used in these calculations. The appropriate data set should meet the following criteria:

$$0.15 C_o V_c/V_t < \bar{C}_w < 0.85 C_o V_c/V_t \tag{8.22}$$

which is equivalent to specifying that only data from flasks where the fraction of chemical adsorbed falls between 0.15 and 0.85 should be used so that $\bar{C}_w$ has been measured reliably. The experiment has been designed so that, in the other flask, either $\bar{C}_w \approx 0.0$ (100% of the chemical was sorbed) or $\bar{C}_w \sim C_o V_c/V_t$ (no measurable sorption occurred).

If the value of K_{oc}^{scr} is less than 1500, no additional sorption measurements are required because sorption on sediments will not be a significant environmental fate. If the value of K_{oc}^{scr} is greater than 1500, the value of C_s should be measured for the sediment in whichever set of flasks gave partial sorption. A new value of K_p^{scr} is calculated:

$$K_p^{scr} = F_{oc} K_{oc}^{scr} = \bar{C}_s/\bar{C}_w \tag{8.23}$$

This value of K_p^{scr} is used to plan the detailed isotherm.

8.7 DETAILED TESTS

8.7.1 Purpose

This detailed sorption isotherm test protocol is intended to measure the value of the sorption partition coefficient, $K_p = K_{oc} F_{oc}$, on natural soils or sediments. Detailed sorption isotherm measurements should be made on a chemical if the value of K_{oc} obtained from the screening test is greater than about 2000.

8.7.2 Procedure

The experimental plan for each isotherm, which should be run on at least three sediments or soils, is shown in Table 8.3. The initial concentration of the chemical in the stock solution should be saturated or 1 mg liter^{-1}, whichever is lower. It is essential to assure that all isotherm measurements are conducted with pure solutions of the chemical in water. Procedures for preparing these solutions are given in Section 8.6.2.

TABLE 8.3. EXPERIMENTAL PLAN FOR THE DETAILED SORPTION ISOTHERM MEASUREMENTS[a]

Concentration of chemical	Number of flask No sediment	 Low sediment	 High sediment
None	1	1	1
Low	1	2	2
High	1	2	2

[a] Four replicate measurements should be made of C_s and C_w at equilibrium in each flask.

Next, the amount of sediment required in each flask must be calculated. The experiments are designed so that the concentration of chemical remaining in solution spans a tenfold concentration range at equilibrium. The equations needed to calculate the amount of stock solution of chemical and stock sediment suspension are

$$F_s = \text{fraction of chemical sorbed} \quad (8.24)$$

$$C_s^{est} = \text{predicted value of } C_s\text{, based on value of } F_s \text{ selected} \quad (8.25)$$

$$= C_o V_c F_s / C_{ss} V_s$$

$$V_s = \frac{V_t F_s}{(1 - F_s) K_p^{scr} C_{ss}} \quad (8.26)$$

$$= \frac{V_t F_s}{(1 - F_s)(K_{oc}^{scr} F_{oc}) C_{ss}} \quad (8.27)$$

The values of F_s and C_s^{est} are selected to span a range of concentrations of both C_s and C_w. These selections then dictate the values of V_s and V_c for each flask. The equations for V_s and V_c for each flask of the detailed isotherm are given in Table 8.4.

TABLE 8.4. CALCULATION OF VOLUMES OF STOCK SOLUTIONS FOR DETAILED ISOTHERM MEASUREMENTS

	No sediment	Low sediment	High sediment
No chemical			
F_s	0	0	0
C_w^{est}	0	0	0
V_s	0	$0.33\ V_t/K_p^{scr}\ C_{ss}$	$3.0\ V_t/K_p^{scr}\ C_{ss}$
V_c	0	0	0
Low chemical			
F_s	0	0.25	0.75
C_w^{est}	$0.4\ C_o$	$0.26\ C_o$	$0.088\ C_o$
V_s	0	$0.33\ V_t/K_p^{scr}\ C_{ss}$	$3.0\ V_t/K_p^{scr}\ C_{ss}$
V_c^l	$0.35\ V_t$	$0.35\ V_t$	$0.35\ V_t$
High chemical			
F_s	0	0.25	0.75
C_w^{est}	$0.6\ C_o$	$0.45\ C_o$	$0.15\ C_o$
V_s	0	$0.33\ V_t/K_p^{scr}$	$3.0\ V_t/K_p^{scr}\ C_{ss}$
V_c^h	$0.6\ V_t$	$0.6\ V_t$	$0.6\ V_t$

The concentration of sediment in the stock sediment suspension, C_{ss} (in g liter^{-1}), must be adjusted, depending on the value of $K_p^{scr} = K_{oc}^{scr}\ F_{oc}$, so that $V_s < 0.4\ V_t$ for the high sediment/low chemical flask. Otherwise, the experiments cannot be carried out. Therefore, C_{ss} must be adjusted so that

$$C_{ss} > \frac{F_s\ V_t}{(K_{oc}^{scr}\ F_{oc})(1 - F_s)\ V_s} = \frac{F_s\ V_t}{K_p^{scr}\ (1 - F_s)\ V_s} \qquad (8.28)$$

If $V_t = 100$ ml, $F_s = 0.8$, $K_p^{scr} = 50$, and $V_s = 0.4\ V_t$, then $C_{ss} > 0.2$ g ml^{-1}.

Blanks are prepared using appropriate volumes of only one stock solution. In all cases, the volume of distilled water that must be added to make up the volume to V_t is

$$V_m = V_t - V_s - V_c \tag{8.29}$$

At least four sediments, spanning a range of organic content, cation exchange capacity, and predominant clay mineral, should be used for detailed isotherm measurements.

All solutions-suspensions, and blanks should be made up in clean 500-ml Erlenmeyer flasks, which are then sealed, covered with aluminum foil, and shaken gently on a wrist-action shaker for 12 to 16 hours. If shorter equilibration times are used, the sorption equilibrium may not be obtained. If longer equilibration times are used, transformation processes, most likely biodegradation, may occur. If biodegradation is observed, which may be the cause of a poor mass balance (see below), a 2-hour equilibration time may be used.

At the end of the equilibration period, the contents of each flask must be centrifuged to separate the sediment from the supernatant. The centrifugation conditions used for the screening isotherm should also be used for the detailed isotherms (see Section 8.6.2).

After centrifuging, the aqueous phase is decanted carefully from the sediment. About 1 ml of solution will probably be retained in the centrifuge tube. One extraction and four replicate analyses of the chemical in the extract must be performed on both the supernatant and sediment from each flask.* Appropriate standard solutions that span the concentration range of the chemical in the extracts must also be analyzed.

A simple check of the mass balance in each flask should be made to determine if significant losses (or gains) of the chemical have occurred. At least 80% of the total amount of chemical (but less than 120%) should be recovered, which is true if equation (8.30) is satisfied:

$$1.2\ C_o V_c \geq C_s C_{ss} V_{ss} + C_w V_t \geq 0.8\ C_o V_c \tag{8.30}$$

If equation (8.30) is not satisfied, the source of the error should be determined and the experiment repeated.

8.7.3 Data Analysis

The data analysis is carried out in two stages. First, a linear least squares regression analysis is performed to estimate K_p for each sediment.

---

* We have presumed that the analytical method developed for the screening isotherm can be used for the sediments used for the detailed isotherms.

The average values of $\bar{C}_w$ and $\bar{C}_s$ for each flask are calculated. The regression equations are:

$$b = \frac{\Sigma x_i y_i}{\Sigma x_i^2} = K_p = K_{oc}\ F_{oc} \tag{8.31}$$

$$S_{yx} = \left\{ \left[\Sigma y_i^2 - \frac{(\Sigma x_i y_i)^2}{\Sigma x_i^2} \right] (n - 1)^{-1} \right\}^{\frac{1}{2}} \tag{8.32}$$

$$95\%\ \text{confidence interval} = (t_{n-1,\alpha}) S_{yx} (\Sigma x_i^2)^{-\frac{1}{2}} \tag{8.33}$$

where $b = K_p$ is the slope, x_i and y_i are the individual or average measurements from each flask of C_w and C_s, respectively, S_{yx} is the standard error, and $t_{n-1,\alpha}$ is the t-value from Student's t-test for n measurements at $\alpha = 0.05$ confidence. These expressions are in the form suitable for use in hand calculators, such as the Hewlett-Packard Model 65. This procedure is used to estimate K_p for each sediment tested.

When both C_s and C_w are measured, the linear least squares procedures using average values for C_s and C_w are not statistically correct because response variables appear on both sides of the regression equation. In addition, the averaging procedure throws away valuable information about experimental variance. To deal more correctly with this situation, we use pairs of simultaneous nonlinear regression equations, one pair for each experimental condition. One of the pair utilizes concentrations of chemical on the sediment, C_s,

$$C_s = \hat{K}_p\ \hat{C}_i \tag{8.34}$$

and the other of the pair utilizes the concentrations measured in the supernatant, C_w,

$$C_w = \hat{C}_i \tag{8.35}$$

where $\hat{C}_i$ is the estimated value of supernatant chemical concentration for a particular experimental condition, i. With this formulation, the response variables appear only on the left-hand side of the regression equation. The common parameters $\hat{K}_p$ and $\hat{C}_i$ tie the simultaneous regressions together and assure that the resulting estimate for K_p is conditioned on both the sediment and supernatant concentrations measured.

The method is superficially similar to the simple linear least squares procedure used to estimate K_p. The regression equation (8.35) use the supernatant concentrations to estimate a single concentration that best represents the concentration in the flasks for each different substrate and sediment level. This representative concentration is then used with the concentration of supernatant on the sediment in equation (8.34) to estimate K_p. An important difference between the two approaches, however, is that, with the nonlinear appraoch, the supernatant concentration, $\hat{C}_i$, that represents a particular substrate and sediment level is not necessarily the average supernatant concentration. The values of C_i determined by the method are almost always very close to the average except when concentration measurements are highly scattered.

An important feature of nonlinear approach is that it does not require that the same number of observations of both C_s and C_w be made in each flask. The formulation also does not require that individual measured values of C_s and C_w from a particular flask be paired. This is an important feature because any pairing of data points is artificial and could bias the estimate of K_p.

The non-linear approach can be formulated compactly if the sorption isotherm experiments are thought of in terms of two factors: total mass of chemical and sediment level. Let the subscript i correspond to a particular combination of sediment level and chemical mass level. For example, a possible experimental setup is shown below in which the numbers represent the value of the test condition identification variable i to be used in the regression procedure described below.

Concentration of chemical	No sediment	Low sediment	High sediment
None	1	4	7
Low	2	5	8
High	3	6	9

In general, suppose there are p total experimental conditions. Each condition may be represented by one or more flasks. Then the regression model may be written as:

$$\hat{Y}_j = \sum_{i=1}^{p} \omega_{ij} \left[\hat{C}_i (1 - \delta_j) + \hat{K}_p \hat{C}_i \delta_j M_s \right] \qquad (8.36)$$

where

$$\delta_j = \begin{cases} 1 \text{ if data are from the sediment} \\ 0 \text{ if data are from the water} \end{cases}$$

$\hat{Y}_j$ = predicted concentration of chemical for observation j, j = 1, ..., n. When $\delta_j = 1$, $\hat{Y}_j$ is the predicted value of the chemical concentration on the sediment. When $\delta_j = 0$, $\hat{Y}_j$ is the predicted value of the chemical concentration in the water phase.

i = test condition identification

$$\omega_{ij} = \begin{cases} 1 \text{ if observation j corresponds to test condition i} \\ 0 \text{ otherwise } i = 1, \ldots, p \end{cases}$$

$\hat{C}_i$ = estimate of chemical concentration in the water phase, corresponding to test condition i

$\hat{K}_p$ = estimate of partition coefficient, $\hat{K}_p > 0$

M_s = grams of sediment per liter of water.

There are then p + 1 parameters to be estimated, C_i (i = 1,...,p) and K_p. Note that there need not be data in all the cells indexed by i. The indicator variables ω_{ij}, if properly specified, will prevent any inconsistencies due to missing observations.

The BMDP3R program (from the Biomedical Computer Programs package, P-series) may be used to obtain the necessary parameter estimates. This program uses a modified Gauss-Newton algorithm (described in Section 8.8.10). Input variables for the BMDP3R routine are Y_j, t_j (the test condition identification), δ_j, and M_s. The ω_{ij} are computed by the program, using the value of t_j ($\omega_{ij} = 1$ for $i = t_j$, 0 otherwise). The BMDP3R program requires (as a minimum) the following cards on the IBM370:

```
(job card)
(key card)
// EXEC BIMEDT, PROG + BMDP3R
// FUN DD *

     DIMENSION IW (50)
     NT = NPAR-1
     F  = 0
     DF(NPAR) = 0
     DO 1 I = 1, NT
     IW(I) = 0
1    CONTINUE
```

```
      ICOND = X(2) + .01
      IDELT = X(3) + .01
      IW(I COND) = 1
      DO 2 I = 1, NT
      F = F + IW(I) * (P(I)*(1-IDELT) + X(4)*P(NPAR)*P(I)*IDELT)
      DF(I) = IW(I)*((1-IDELT) + X(4)*P(NPAR)*IDELT)
      DF(NPAR) = DF(NPAR) + IW(I)*X(4)P(I)*IDELT

2     CONTINUE
      /GO.SYSIN             DD *
      /PROBLEM              TITLE = ' ⟨problem title⟩'  .
      /INPUT                VARIABLES ARE 4 .
                            FORMAT IS '(⟨input format⟩)'.
      /VARIABLES            NAMES ARE CONC, TCODE, SOURCE, MASS .
      /REGRESSION           DEPENDENT IS CONC .
                            INDEPENDENT ARE TCODE, SOURCE, MASS .
                            PARAMETERS = ⟨p+1⟩  .
      /PARAMETERS           INITIAL = ⟨p⟩ * 0.0, ⟨initial estimate of Kp⟩ .
                            Minimum = ⟨p+1⟩* 0.0
      /END
      ⟨formatted data goes here⟩
      /*
```

Note: The variables must be input in the order shown for the function to be properly evaluated.

The information within the angle brackets (⟨ ⟩) is to be replaced by the information specific to an individual run of the program. The brackets themselves are not typed.

An example of the computer input stream and output listing corresponding to the input shown above is given on the following pages. Note that data are available only for six cells (2, 3, 5, 6, 8, and 9). The output listing shows that the estimates for the parameters corresponding to empty cells are zero. Obviously, these cells could have been omitted entirely from the model, but they are included for illustrative purposes.

In this example of an input stream, the name card has been included to give meaningful names to the parameters. If this card is omitted, the parameters are referred to in the output as P(1), P(2), and so on where the numbers in parentheses correspond to the cell identification code, and P(p + 1) corresponds to K_p. The names used here identify the sediment level (second character) and the chemical level (third character). For example, CLH corresponds to low sediment concentration and high chemical concentration.

The first several cards of the input (those beginning with "//") may differ at various installations and various modes of input (this run was submitted through a time-sharing terminal).

```
// JOB
// EXEC BIMEDT,PROG=BMDP3R
//FUN DD *
      DIMENSION IW(10)
      NT=NPAR-1
      F=0
      DF(NPAR)=0
      DO 1 I=1,NT
      IW(I)=0
1     CONTINUE
      ICOND=X(2)+.01
      IDELT=X(3)+.01
      IW(ICOND)=1
      DO 2 I=1,NT
      F=F+IW(I)*(P(I)*(1-IDELT)+X(4)*P(NPAR)*P(I)*IDELT)
      DF(I)=IW(I)*((1-IDELT)+X(4)*P(NPAR)*IDELT)
      DF(NPAR)=DF(NPAR)+IW(I)*X(4)*P(I)*IDELT
2     CONTINUE
//GO.SYSIN DD *
/PROBLEM     TITLE IS 'EXAMPLE OF STRUCTURAL REGRESSION'.
/INPUT       VARIABLES ARE 4.
             FORMAT IS '(F11.0,F1.0,F1.0,F9.0)'.
/VARIABLES   NAMES ARE CONC,TCODE,SOURCE,MASS.
/REGRESSION  DEPENDENT IS CONC.
             INDEPENDENT ARE TCODE,SOURCE,MASS.
             PARAMETERS=10.
/PARAMETER   INITIAL= 0,0,0,0,0,0,0,0,1.0.
             MINIMUM=0,0,0,0,0,0,0,0,0,0.
             NAMES ARE C00,C0L,C0H,CL0,CLL,CLH,CH0,CHL,CHH,K.
/END
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     26.600 300.0
     26.300 300.0
     23.600 300.0
     23.100 300.0
     21.800 300.0
     25.600 300.0
     25.100 300.0
     24.700 300.0
     24.700 300.0
     23.400 300.0
     22.500 300.0
     10.100 200.0
      9.820 200.0
     10.100 200.0
      9.960 200.0
      9.960 200.0
      9.960 200.0
     14.300 200.0
     13.900 200.0
     14.000 200.0
     13.500 200.0
     13.500 200.0
     13.100 200.0
     20.000 600.0000358
     17.800 600.0000358
     14.900 600.0000358
     14.900 600.0000358
     14.500 600.0000358
     13.500 600.0000358
```

INPUT STREAM, page 1

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13.500 600.0000358
13.400 600.0000358
14.700 600.0000358
14.300 600.0000358
14.800 600.0000358
16.200 600.0000358
16.000 600.0000358
15.900 600.0000358
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 6.7304610.0000358
 7.8402610.0000358
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 8.380 900.0000717
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 7.940 900.0000717
 7.690 900.0000717
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 5.710 800.0000717
 4.620 800.0000717
 4.4813810.0000717
```

INPUT STREAM, page 2

```
BMDP3R - NONLINEAR REGRESSION
HEALTH SCIENCES COMPUTING FACILITY                          PROGRAM REVISED DECEMBER 1977
UNIVERSITY OF CALIFORNIA, LOS ANGELES                       MANUAL DATE  --  1977
COPYRIGHT (C) 1977, THE REGENTS OF THE UNIVERSITY OF CALIFORNIA

IN THIS VERSION OF BMDP3R

   -- THE FORM OF SPECIFYING LINEAR CONSTRAINTS HAS BEEN CHANGED, SEE BMDP-77 MANUAL PAGE 480.
   -- COMPUTATIONS ARE NOW PERFORMED IN DOUBLE PRECISION.
      IF YOU USE SUBROUTINE FUN BE SURE ALL FUNCTION REFERENCES ARE IN DOUBLE PRECISION.
   -- DEFAULT TOLERANCE FOR PIVOTING IS NOW .00000001.


 PROGRAM CONTROL INFORMATION

       /PROBLEM    TITLE IS 'EXAMPLE OF STRUCTURAL REGRESSION'.
       /INPUT      VARIABLES ARE 4.
                   FORMAT IS '(F11.0,F1.0,F1.0,F9.0)'.
       /VARIABLES  NAMES ARE CONC,TCODE,SOURCE,MASS.
       /REGRESSION DEPENDENT IS CONC.
                   INDEPENDENT ARE TCODE,SOURCE,MASS.
                   PARAMETERS=10.
       /PARAMETER  INITIAL= 0,0,0,0,0,0,0,0,1.0.
                   MINIMUM=0,0,0,0,0,0,0,0,0,0.
                   NAMES ARE C00,COL,COH,CLO,CLL,CLH,CHO,CHL,CHH,K.
       /END


 PROBLEM TITLE . . . . . . .EXAMPLE OF STRUCTURAL REGRESSION

 NUMBER OF VARIABLES TO READ IN. . . . . . . . .        4
 NUMBER OF VARIABLES ADDED BY TRANSFORMATIONS. .        0
 TOTAL NUMBER OF VARIABLES . . . . . . . . . . .        4
 NUMBER OF CASES TO READ IN. . . . . . . . . . . 1000000
 CASE LABELING VARIABLES . . . . . . . . . . . .
 LIMITS AND MISSING VALUE CHECKED BEFORE TRANSFORMATIONS
 BLANKS ARE. . . . . . . . . . . . . . . . . . .  ZEROS
 INPUT UNIT NUMBER . . . . . . . . . . . . . . .        5
 REWIND INPUT UNIT PRIOR TO READING. . DATA. . .       NO

 INFUT FORMAT
       (F11.0,F1.0,F1.0,F9.0)


 VARIABLES TO BE USED
           1  CONC          2  TCODE          3  SOURCE         4  MASS
```

OUTPUT LISTING, page 1

```
REGRESSION TITLE

REGRESSION NUMBER . . . . . . . . . . . . . . . . .        0
INDEPENDENT VARIABLE(FOR BUILT-IN FUNCTION) . .    TCODE
DEPENDENT VARIABLE. . . . . . . . . . . . . . . .    CONC
WEIGHTING VARIABLE. . . . . . . . . . . . . . . .
NUMBER OF PARAMETERS. . . . . . . . . . . . . . .       10
NUMBER OF CONSTRAINTS . . . . . . . . . . . . . .        0
TOLERANCE FOR PIVOTING. . . . . . . . . . . . . . 0.00000001000
TOLERANCE FOR CONVERGENCE . . . . . . . . . . . . 0.00001000000
MAXIMUM NUMBER OF ITERATIONS. . . . . . . . . . .       50
MAXIMUM NUMBER OF INCREMENT HALVINGS. . . . . . .        5
NUMBER OF DATA PASSES PER CASE. . . . . . . . . .        1
COMPUTE LOSS FUNCTION . . . . . . . . . . . . . .       NO

USING THE ABOVE SPECIFICATIONS THIS PROGRAM COULD PROCESS 1602 CASES.

NUMBER OF CASES READ. . . . . . . . . . . . . . .       83

VARIABLE                           STANDARD
NO. NAME           MEAN            DEVIATION        MINIMUM         MAXIMUM

 1  CONC         11.492186          6.573570        3.866400       27.599991
 2  TCODE         5.626487          2.423011        2.000000        9.000000
 3  SOURCE        0.108433          0.312817        0.0             1.000000
 4  MASS          0.000037          0.000028        0.0             0.000072

PARAMETER MAXIMA. . . . . . . . . . . . ************** ************** ************** ************** ************** **************

PARAMETER MINIMA. . . . . . . . . . . .       0.0            0.0            0.0            0.0            0.0            0.0

ITERATION  INCREMENT   RESIDUAL SUM
 NUMBER    HALVINGS     OF SQUARES          C00            C0L            C0H            CL0            CLL            CLH

    0          0        14314.491725        0.0            0.0            0.0            0.0            0.0            0.0
    1          0        11991.323534        0.0           11.850000      24.583326       0.0            7.779166      15.314284
    2          0          132.412801        0.0           11.850000      24.583326       0.0            7.858546      15.353870
    3          0          132.137624        0.0           11.850000      24.583326       0.0            7.828097      15.349891
    4          0          132.137374        0.0           11.850000      24.583326       0.0            7.826832      15.349106
    5          0          132.137373        0.0           11.850000      24.583326       0.0            7.826827      15.349111
    6          0          132.137373        0.0           11.850000      24.583326       0.0            7.826826      15.349110
    7          0          132.137373        0.0           11.850000      24.583326       0.0            7.826826      15.349110

PARAMETER MAXIMA. . . . . . . . . . . . ************** ************** ************** **************
PARAMETER MINIMA. . . . . . . . . . . .       0.0            0.0            0.0            0.0

ITERATION  INCREMENT   RESIDUAL SUM
 NUMBER    HALVINGS     OF SQUARES          CH0            CHL            CHH             K

    0          0        14314.491725        0.0            0.0            1.000000        0.0
    1          0        11991.323534        0.0            4.767500       8.457500    89450.489798
    2          0          132.412801        0.0            4.787937       8.289340    12614.431253
    3          0          132.137624        0.0            4.788242       8.322186    12251.348745
    4          0          132.137374        0.0            4.787778       8.326066    12247.249431
    5          0          132.137373        0.0            4.787780       8.326131    12246.909117

    6          0          132.137373        0.0            4.787779       8.326135    12246.903404
    7          0          132.137373        0.0            4.787779       8.326135    12246.903082
```

OUTPUT LISTING, page 2

```
ASYMPTOTIC CORRELATION MATRIX OF THE PARAMETERS


                  COO         COL         COH         CLO         CLL         CLH         CHO         CHL         CHH
                      1           2           3           4           5           6           7           8           9
COO        1     0.0
COL        2     0.0         1.0000
COH        3     0.0         0.0         1.0000
CLO        4     0.0         0.0         0.0         0.0
CLL        5     0.0         0.0         0.0         0.0         1.0000
CLH        6     0.0         0.0         0.0         0.0         0.0106      1.0000
CHO        7     0.0         0.0         0.0         0.0         0.0         0.0         0.0
CHL        8     0.0         0.0         0.0         0.0         0.0047      0.0086      0.0         1.0000
CHH        9     0.0         0.0         0.0         0.0         0.0157      0.0285      0.0         0.0128      1.0000
K         10     0.0         0.0         0.0         0.0        -0.0765     -0.1383      0.0        -0.0621     -0.2057


                  K
                     10

K         10     1.0000

RESIDUAL MEAN SQUARE          1.7386493683

DEGREES OF FREEDOM            76

PARAMETER       ESTIMATE       ASYMPTOTIC          TOLERANCE
                            STANDARD DEVIATION

COO                0.0            0.0           0.0
COL               11.850000       0.380641      1.0000000000
COH               24.503326       0.380641      1.0000000000
CLO                0.0            0.0           0.0
CLL                7.826926       0.372903      0.9941558838
CLH               15.349110       0.348716      0.9308658361
CHO                0.0            0.0           0.0
CHL                4.787779       0.369685      0.9961420298
CHH                8.326135       0.366143      0.9576867223
K              12246.903082     972.840332      0.9315822721

IF A PARAMETER LIES ON THE BOUNDARY IT IS ASSIGNED A STANDARD DEVIATION OF ZERO
```

OUTPUT LISTING, page 3

```
 CASE
NO. LABEL        PREDICTED    STD DEV OF    OBSERVED
                  CONC        PRED VALUE     CONC        RESIDUAL      TCODE       SOURCE       MASS

  1              24.583313    0.380641     27.599991     3.016665    3.000000    0.0          0.0
  2              24.583313    0.380641     26.599991     2.016665    3.000000    0.0          0.0
  3              24.583313    0.380641     26.299988     1.716661    3.000000    0.0          0.0
  4              24.583313    0.380641     23.599991    -0.983335    3.000000    0.0          0.0
  5              24.583313    0.380641     23.099991    -1.483335    3.000000    0.0          0.0
  6              24.583313    0.380641     21.799988    -2.783338    3.000000    0.0          0.0
  7              24.583313    0.380641     25.599991     1.016665    3.000000    0.0          0.0
  8              24.583313    0.380641     25.099991     0.516665    3.000000    0.0          0.0
  9              24.583313    0.380641     24.699997     0.116671    3.000000    0.0          0.0
 10              24.583313    0.380641     24.699997     0.116671    3.000000    0.0          0.0
 11              24.583313    0.380641     23.399994    -1.183331    3.000000    0.0          0.0
 12              24.583313    0.380641     22.500000    -2.083325    3.000000    0.0          0.0
 13              11.849999    0.380641     10.099999    -1.750000    3.000000    0.0          0.0
 14              11.849999    0.380641      9.820000    -2.030000    2.000000    0.0          0.0
 15              11.849999    0.380641     10.099999    -1.750000    2.000000    0.0          0.0
 16              11.849999    0.380641      9.959999    -1.890000    2.000000    0.0          0.0
 17              11.849999    0.380641      9.959999    -1.890000    2.000000    0.0          0.0
 18              11.849999    0.380641      9.959999    -1.890000    2.000000    0.0          0.0
 19              11.849999    0.380641     14.299999     2.449999    2.000000    0.0          0.0
 20              11.849999    0.380641     13.900000     2.049999    2.000000    0.0          0.0
 21              11.849999    0.380641     14.000000     2.150000    2.000000    0.0          0.0
 22              11.849999    0.380641     13.500000     1.650000    2.000000    0.0          0.0
 23              11.849999    0.380641     13.500000     1.650000    2.000000    0.0          0.0
 24              11.849999    0.380641     13.099999     1.249999    2.000000    0.0          0.0
 25              15.349110    0.348716     20.000000     4.650889    6.000000    0.0          0.0
 26              15.349110    0.348716     17.799988     2.450877    6.000000    0.0          0.000036
 27              15.349110    0.348716     14.900000    -0.449111    6.000000    0.0          0.000036
 28              15.349110    0.348716     14.900000    -0.449111    6.000000    0.0          0.000036
 29              15.349110    0.348716     14.500000    -0.849110    6.000000    0.0          0.000036
 30              15.349110    0.348716     13.500000    -1.849110    6.000000    0.0          0.000036
 31              15.349110    0.348716     13.500000    -1.849110    6.000000    0.0          0.000036
 32              15.349110    0.348716     13.400000    -1.949110    6.000000    0.0          0.000036
 33              15.349110    0.348716     14.700000    -0.649111    6.000000    0.0          0.000036
 34              15.349110    0.348716     14.299999    -1.049110    6.000000    0.0          0.000036
 35              15.349110    0.348716     14.799999    -0.549111    6.000000    0.0          0.000036
 36              15.349110    0.348716     16.199997     0.850886    6.000000    0.0          0.000036
 37              15.349110    0.348716     16.000000     0.650889    6.000000    0.0          0.000036
 38              15.349110    0.348716     15.900000     0.550889    6.000000    0.0          0.000036
 39               6.729650    0.535288      6.730399     0.000749    6.000000    0.0          0.000036
 40               6.729650    0.535288      6.730399     0.000749    6.000000    1.000000     0.000036
 41               6.729650    0.535288      7.840199     1.110549    6.000000    1.000000     0.000036
 42               8.326135    0.366143      8.639999     0.313865    6.000000    1.000000     0.000036
 43               8.326135    0.366143      8.910000     0.583865    9.000000    0.0          0.000072
 44               8.326135    0.366143      8.379999     0.053864    9.000000    0.0          0.000072
 45               8.326135    0.366143      8.110000    -0.216135    9.000000    0.0          0.000072
 46               8.326135    0.366143      8.379999     0.053864    9.000000    0.0          0.000072
 47               8.326135    0.366143      8.110000    -0.216135    9.000000    0.0          0.000072
 48               8.326135    0.366143      9.179999     0.853864    9.000000    0.0          0.000072
 49               8.326135    0.366143      9.179999     0.853864    9.000000    0.0          0.000072
 50               8.326135    0.366143      8.910000     0.583865    9.000000    0.0          0.000072
 51               8.326135    0.366143      8.059999    -0.266135    9.000000    0.0          0.000072
 52               8.326135    0.366143      7.940000    -0.386135    9.000000    0.0          0.000072
 53               8.326135    0.366143      7.690000    -0.636135    9.000000    0.0          0.000072
 54               7.311202    0.603195      6.725499    -0.585704    9.000000    1.000000     0.000072
 55               7.311202    0.603195      6.101700    -1.209502    9.000000    1.000000     0.000072
```

OUTPUT LISTING, page 4

```
 56           7.826825   0.372903   7.740000  -0.086826   5.000000   0.0        0.000036
 57           7.826825   0.372903   7.349999  -0.476826   5.000000   0.0        0.000036
 58           7.826825   0.372903   7.740000  -0.086826   5.000000   0.0        0.000036
 59           7.826825   0.372903   7.809999  -0.016826   5.000000   0.0        0.000036
 60           7.826825   0.372903   7.679999  -0.146827   5.000000   0.0        0.000036
 61           7.826825   0.372903   7.419999  -0.406827   5.000000   0.0        0.000036
 62           7.826825   0.372903   8.639999   0.813173   5.000000   0.0        0.000036
 63           7.826825   0.372903   8.509999   0.683173   5.000000   0.0        0.000036
 64           7.826825   0.372903   8.639999   0.813173   5.000000   0.0        0.000036
 65           7.826825   0.372903   7.320000  -0.506826   5.000000   0.0        0.000036
 66           7.826825   0.372903   7.320000  -0.506826   5.000000   0.0        0.000036
 67           7.826825   0.372903   7.179999  -0.646827   5.000000   0.0        0.000036
 68           3.431586   0.306956   3.866400   0.434813   5.000000   1.000000   0.000036
 69           3.431586   0.306956   3.866400   0.434813   5.000000   1.000000   0.000036
 70           3.431586   0.306956   3.866400   0.434813   5.000000   1.000000   0.000036
 71           4.787779   0.369685   4.290000  -0.497779   8.000000   0.0        0.000072
 72           4.787779   0.369685   4.290000  -0.497779   8.000000   0.0        0.000072
 73           4.787779   0.369685   4.150000  -0.637780   8.000000   0.0        0.000072
 74           4.787779   0.369685   5.160000   0.372221   8.000000   0.0        0.000072
 75           4.787779   0.369685   4.900000   0.112220   8.000000   0.0        0.000072
 76           4.787779   0.369685   4.900000   0.112220   8.000000   0.0        0.000072
 77           4.787779   0.369685   4.580000  -0.207779   8.000000   0.0        0.000072
 78           4.787779   0.369685   4.580000  -0.207779   8.000000   0.0        0.000072
 79           4.787779   0.369685   4.450000  -0.337779   8.000000   0.0        0.000072
 80           4.787779   0.369685   5.580000   0.792221   8.000000   0.0        0.000072
 81           4.787779   0.369685   5.709999   0.922220   8.000000   0.0        0.000072
 82           4.787779   0.369685   4.620000  -0.167779   8.000000   0.0        0.000072
 83           4.204163   0.451044   4.481299   0.277137   8.000000   1.000000   0.000072
SERIAL CORRELATION   0.63385
```

OUTPUT LISTING, page 5

The output listing shows that, even for a very poor initial guess for K_p (the guess was zero and the actual estimate was 12,247), the sequence converged in only seven iterations (page 2 of the output listing), at a total computer cost of 73¢. Page 3 of the output summarizes the parameter estimates and the estimated asymptotic standard deviations of the estimates. The latter may be used to construct confidence intervals for the parameters (assuming normality). Pages 4 and 5 of the output list the input data, the predicted values, and the residuals.

The refined values of K_p for the soils or sediments tested can then be used to estimate a K_{oc} value for the chemical. The linear least squares approach embodied in equations (8.31), (8.32), and (8.33) is used where y is identified as the measured values of K_p and X is identified as F_{oc}. Solution to the linear least squares regression yields a value of b that is identified as K_{oc}.

8.8 BACKGROUND

Sorption of organic substrates onto sediments and biota can be a very important phenomenon in the aquatic environment. The sediments can act as sinks for sorbed materials, removing them from the water column. However, the substrate can also be released (desorbed) from the sediments at a later time. In this way sorbed material can also be a source of pollution. Sorption of pollutants by sediments can also be a source of pollution. Sorption of pollutants by sediments often results in the concentration of low solubility pollutants in a part of the water column where uptake by a biomagnification becomes significant, as has been the case with Kepone in the James River and in Chesapeake Bay.

The use of the terms "sorption" and "adsorption" deserves special comment. Sorption includes any type of process whereby the substrate is physically or chemically bound to a solid surface (chemisorption). Adsorption implies to us that the process that holds the substrate on the sediment is strictly physical, such as the van der Waals type of attraction. However, sorption processes of ionizable substrates such as amines may include chemical bonding interactions as well as physical processes. While other authors have used adsorption to include chemical interactions (Hamaker and Thompson, 1972) we will use "sorption" to avoid confusion.

Several excellent reviews of the sorption of organic substrates on soils and sediments are available. Hamaker and Thompson (1972) have prepared an excellent review of sorption of pesticides on soil, clay, sediments, and the like. Theng (1974) has written a prize-winning text entitled The Chemistry of Clay-Organic Reactions. This section provides only a brief overview of sorption on soils. The reader should consult the two references cited above for detailed discussions.

8.8.1 Theory

Sorption takes place, in general, when solution containing a dissolved chemical contacts a solid phase surface. If the total amount of chemical is increased, the amount of chemical that is sorbed is also increased. Experimental data have generally been found to fit one of two mathematical forms: the Langmuir and Freundlich isotherms.

The Langmuir isotherm can be derived theoretically from kinetic considerations by assuming that:

- The energy of sorption is constant for a particular sorbent and independent of the surface coverage.
- Sorbed molecules do not interact.
- Sorbed molecules form a monolayer on the sorbent surface; the amount sorbed is limited by the surface area of the sorbent.

First, we define C_w and C_s as

$$C_w = \frac{\text{weight substrate in solution } (\mu g)}{\text{ml solution}} = \text{ppm}$$

$$C_s = \frac{\text{weight substrate sorbed } (\mu g)}{\text{g sorbent}} = \text{ppm}$$

at equilibrium. The substrate weights must be in the same units (e.g., ng, μg). The Langmuir isotherm equation is defined as

$$C_s = \frac{a\ b\ C_w}{1 + b\ C_w} \tag{8.37}$$

where a and b are constants and

$$a = X_c \tag{8.38}$$

$$b = \frac{K_p}{X_c} \tag{8.39}$$

where X_c is the sorption capacity of the sorbent and K_p is a partition coefficient. Equation (8.37) can be rewritten as

$$C_s = \frac{K_p C_w}{1 + K_p C_w / X_c} \tag{8.40}$$

or

$$C_s = \frac{X_c\ K_p\ C_w}{X_c + K_p C_w} \tag{8.41}$$

Data for gas-solid sorption generally and for organic substrates sorbed on clay minerals usually fit the Langmuir isotherm. However, natural sediments are inhomogeneous--sorbed complex organic materials such as humic substances are already present on the clay particles--and sorption by these sediments usually fails to fit the Langmuir isotherm because the first assumption is violated.

Data for sorption of multiple substrates from solution on nonuniform surfaces generally fit the Freundlich isotherm, which is an empirical equation

$$C_s = K\,C_w^{1/n} \tag{8.42}$$

where K and n are experimentally determined constants,* and again, it is assumed implicitly that the system is at equilibrium.

At low substrate concentrations, n is often very nearly equal to 1. If n = 1, the units on each side of equation (8.42) cancel and K becomes a partition coefficient, as defined by

$$C_s = K_p\,C_w \tag{8.43}$$

Since sorption of organic molecules is often correlated with soil and sediment fraction organic content (F_{oc}) (see Section 8.7), a useful form of equation (8.43) can be defined as

$$C_s = K_{oc}\,C_w \tag{8.44}$$

where

$$K_{oc} = K_p/F_{oc} \tag{8.45}$$

The F_{oc} can be measured by several analytical procedures (Hesse, 1971).

8.8.2 Sorption Mechanism

Sorption of a chemical (the sorbate) onto a solid surface (the sorbent) is due to the intermolecular forces between the sorbate and sorbent. In the case of sorption of organic chemicals dissolved in water on natural sediment sorbents, many types of interactions are possible, including:

- Van der Waals/London forces.
- Hydrophobic bonding induced by the unusual lattice structure of liquid water.
- Charge transfer, including Π-cloud and lone electron-pair donors and acceptors, and hydrogen bonding.
- Ligand exchange and chelation, ion exchange, and other forms of chemisorption.

---

*Hamaker and Thompson (1972) also point out that the exponent in equation (8.42), 1/n, is an "archaic remnant of an attempt to give the Freundlich equation physical meaning and is retained only because its use is embedded in the literature."

Van der Waals-type interactions arise as a result of very rapid fluctuations in the charge distribution of the electron clouds of molecules that induce an instantaneous dipole that averages out on longer times. On a molecular level, however, the instantaneous dipole results in weak attractive forces that decrease as a function of d^{-6}, where d is the distance between molecules. At distances less than the van der Waals radii, strong repulsive forces produced by the nuclear charge limit the distance of approach.

Liquid water is considered to be a combination of ice-like structures and more compact but random orientations of water molecules within and around the ice-like structure. The hydrophobic portions of dissolved organic molecules disrupt the structure of liquid water and raise the entropy of the solution. If sorption is possible, the water is able to revert back to its normal structure, thereby reducing the entropy of the system. Hence, sorption is thermodynamically favored. This sorption mechanism has been called hydrophobic bonding. The combination of van der Waals and hydrophobic bonding may be largely responsible for the strong sorption characteristics of chlorinated organic molecules such as DDT (Hamaker and Thompson, 1972), disulfotone (Graham-Bryce, 1967), and high molecular weight polynuclear organic molecules (POMs) on soils (Smith et al., 1978).

Charge transfer reactions, such as π electron donation by aromatics and lone-pair interactions of amines, may be important interaction mechanisms with soil and sediment organic matter. However, formation of charge-transfer complexes is also an equilibrium process

$$A + D = A \cdot D \text{ (complex)}$$

and, at the very low concentrations of organic pollutants found in the environment, the equilibrium should lie far to the left.

Chemisorption, which may include ligand exchange, chelation, and ion exchange may be very important processes, especially with ionizable substrates such as carboxylic acids and amines. An excellent example is the herbicide paraquat, 1,1'-dimethyl-4,4'-bipyridylium ion, which possesses two permanent positive charges. It is strongly sorbed (or, more correctly, chemisorbed) to the cation exchange sites of clays and sediments (Karickhoff and Brown, 1977; Hamaker and Thompson, 1972).

8.8.3 General Design of Sorption Isotherm Measurements

The general procedure for measuring sorption isotherms consists of equilibrating a solution of the chemical with the sediment for a period of hours. Then C_w and sometimes C_s is measured by an appropriate analytical technique. The concentration of chemical and/or sediment is adjusted so that C_w spans a reasonable range, say, from a factor of 2 to more than 10.

To fit the isotherm data to the Freundlich isotherm equation, a plot of C_s versus C_w (for $n \neq 1$) is prepared. The slope of the line is K_p. If the exponential form is used ($n = 1$), a plot of log C_s versus log C_w should be a line with slope 1/n and log C_s = K when log C_w = 1. Statistical procedures for calculating K_p or 1/n and K are described in Sections 8.7.3 and 8.8.10.

Several experimental designs are possible to obtain data over a range of values of C_w. One approach is to vary the total amount of chemical present and hold the sediment loading constant. Then the fraction of the chemical adsorbed, F_s, will be nearly constant. Two major advantages of this approach are that it is relatively convenient to set up and that saturation effects can be observed if C_w is high enough. An alternative approach is to hold the total concentration of chemical constant and vary the sediment loading. This second approach has the advantage that, if the value of K or K_p is affected by the sediment loading, the effect can be observed. Either of these approaches will be unsatisfactory if the solubility of the chemical is very low or the precision and accuracy of the analytical are poor.

When sediment loading is held constant and total chemical concentration is varied, C_s will be low at low total chemical concentrations. When the total chemical concentration is held constant and sediment loading is varied, then at the low sediment loadings, the amount of chemical adsorbed will be low and $C_s \approx 0$. Similarly, at the high sediment loadings, most of the chemical will be on the sediment and $C_w \approx 0$. If the accuracy and precision of the measurement of C_s and C_w are poor at very low levels, the precision of the estimates of K or K_p will also be very low.

For these reasons, we recommend the experimental design suggested in Table 8.3, which is a combination of the two approaches. The levels of sediment and chemical have been adjusted to span a range of C_w of a factor of about 4 (see Table 8.4).

Many of the isotherm measurements reported in the literature are based on measurements of C_w only, plus the known total amount of chemical and sediment added. This approach is particularly convenient when radio-labeled samples of the chemical are available. However, our experience with sorption isotherm measurements suggests that direct, independent measurement of C_s and C_w is essential to obtain accurate and precise estimates of K or K_p. If both C_s and C_w are measured, losses due to sorption on the walls of the vessel, volatilization, and chemical and biological transformation processes will be detected when low mass balances are observed. The statistical procedures recommended in this protocol are not affected by such losses, and estimates of K or K_p can be obtained (unless C_s = 0 or C_w = 0).

The remaining subsections address specific problems that arise when one attempts to design a suitable test protocol for determining the sorption and desorption of organic chemicals by sediments. The most important questions involve the kinetics of sorption and desorption, the effects of sediment particle size, equilibration time, system pH, indigenous dissolved organics, and the use of natural wet or dried sediments. Experimental work has been done in these areas, and the results are available from various sources. Unfortunately, little attention has been given to the detailed reporting of experimental procedures.

8.8.4 Sediment Particle Size

Sediment particle size is an important parameter in the description of an experimental protocol because there is considerable evidence that the value of K_p varies strongly with the size fraction of a particular soil or sediment sample. Experimentally, it would be very convenient to use only particles less than 100 μm in diameter. The work done in this area indicates that the large particles will not significantly affect sorption characteristics of the sediment. Meyers and Quinn (1973) fractionated clays and natural sediments into five sizes ranging from 1 mm to less than 44 μm. They found that the 1-mm to 250-μm fractions sorbed essentially no heptadecanoic acid and that the 250 to 105-μm fractions sorbed only 1% of the acid sorbed by the fractions smaller than 105 μm.

Karickhoff and Brown (1977) studied the sorption of paraquat on natural sediments that had been fractionated by size. The experiment suffers from low total recovery of the paraquat (54% - 90%). It was noted, however, that the low paraquat recovery was due mostly to the loss of small particles that had been retained on the larger particles after the first separation and were later washed away. Because the low recovery is due primarily to the loss of fine particles, the data for the larger particles should still be useful. It was found that only 1% - 9% of the total sorbed paraquat was on the particles larger than 64 μm in diameter.

It has been shown by Huang et al. (1974), Wang et al. (1972), Pierce et al. (1973), Karickhoff et al. (1978), and Saltzman et al. (1971), that increased sorption occurs in sediments with an increased CEC or organic carbon content, depending on the nature of the sorbate. The greater sorption on small particles is due primarly to their large ratio of surface area to mass. A larger surface area will provide more sites on which sorption can occur. To cite one example, Karickhoff and Brown (1977) measured the CEC and organic carbon content of the various fractions. They found that the CEC and the organic carbon content were greater for smaller particles.

Another potential problem concerning sediment particle size is that very small particles are difficult to remove from suspension. Karickhoff and Brown (1977), using natural clay sediments, found that after 4 hours of centrifugation at 10,000 rpm, the paraquat absorption spectrum of the supernatant was still dominated by sorbed paraquat, indicating that the presence of paraquat in the supernatant is due mostly to a fine clay (>0.08 μm), which is only very slowly removed from suspension. Consequently, care should be taken to determine that all the particles are removed from suspension.

For most natural soils and sediments, the fine clay fraction represents a small percentage of the total soil or sediment mass. Thus, although Karickhoff and Brown (1977) found that the partition coefficient for paraquat, K_p, was extremely large for the fine clay, for the five natural sediments they tested, less than 0.5% of the total amount sorbed was in the fine clay fraction. Most of the sorption occurred on coarse clay $0.2\ \mu m \leq d \leq 2\ \mu m$. They also found that more than 99% of the paraquat was sorbed by particles larger than 0.08 μm (8×10^{-6} cm). Their data for one natural sediment are shown in Table 8.5. The sorption of paraquat is strongly dependent on the CEC.

TABLE 8.5 PARAQUAT DISTRIBUTION IN A NATURAL SEDIMENT[a]

Fraction	Size range (cm x 10^4)	Sediment fraction (g)	Sediment fraction (%)	Paraquat on sediment fraction (mg)	Paraquat on sediment fraction (%)
Sand	>64	833	88.7	0.7	3.1
Coarse silt	64-20	45	4.8	0.9	4.0
Medium silt	20-5	32	3.4	1.8	8.0
Fine silt	5-2	14	1.5	4.6	20.4
Coarse clay	2-0.2	14	1.5	14.1	62.5
Medium clay	0.2-0.08	0.53	0.06	0.4	1.8
Fine clay	<0.08	0.40	0.04	0.06	0.3

[a] Karickhoff and Brown (1977). The data are for Georgia local stream I.

Karickhoff et al. (1978) also studied nonpolar organics, which have K_p values that are strongly correlated with F_{oc}. An example of this data is given in Table 8.6.

TABLE 8.6 PYRENE DISTRIBUTION IN A NATURAL SEDIMENT[a]

Fraction	Size range (cm x 10^4)	K_p	Sediment fraction (%)	Calculated pyrene on sediment fraction (%)
Sand	>64	42	50	1.8
Coarse silt	64-20	3000	50	96.9
Medium silt	20-5	2500		
Fine silt	5-2	1500		
Clay	<2	1400	1	1.2

[a] Data for Hickory Hill sediment; Karickhoff et al. (1978).

The data in these references suggest that most of a chemical by weight, will be sorbed on the silt and coarse clay fractions of the sediment.

8.8.5 Prediction of Soil or Sediment Partition Coefficients

The most convincing basis for predicting sediment partition coefficients is contained in an extensive review by Kenaga and Goring (1978). They collected data from more than 100 sources on the partition coefficients, solubilities, and octanol-water partition coefficients for a wide variety of organic chemicals. Included were compounds that are neutral, anionic, or cationic in solution. All partition coefficients were converted to K_{oc} values, and K_{oc} was correlated with compound solubility and with octanol-water partition coefficients. Low water solubilities and high octanol-water partition coefficients were associated with large values of K_{oc}. It was found that K_{oc} could be predicted within an order of magnitude from either the solubility or the octanol-water partition coefficient. These results are quite similar to correlations found by Smith et al. (1978) and Karickhoff and Brown (1978). A more complete correlation of K_{oc} versus water solubility using all three sets of data was presented earlier as Figure 8.1 and equation (8.4).

It is not possible to completely explain the success of the correlation, since the chemicals involved probably do not all interact with the soil by the same mechanism. The various interactions probably include van der Waals-London interactions, hydrophobic bonding, hydrogen bonding, charge transfer, ligand exchange, ion exchange, and chemisorption. A partial explanation may be simply that soil and sediment organics (humic and fulvic acid) are complex materials that contain enough different chemical groups that they can interact in all of the above ways with dissolved organic chemicals. Humic material appears to be a highly aromatic polymer that contains carboxyl, phenolic, alcoholic, carbonyl, and methoxyl groups, as well as amino acids and polysaccharides (Schnitzer and Khan, 1972).

An additional factor is that both solubility and K_{ow} indicate how much affinity a particular chemical has for water. Low solubility or a large octanol-water partition coefficient indicates that the chemical is adverse to water, and since humic material is so chemically heterogeneous, it provides an almost universal other place to be.

8.8.6 Equilibration Time

The length of time required for a sorption system to come to equilibrium is another point that needs to be considered. In most cases there will be an initial rapid approach to sorption equilibrium (1-24 hours), followed, in some cases, by a prolonged, slow (+ 4 days) increase in sorption. Doehler and Young (1960) found that quinoline reached approximately 97% of its equilibrium concentration within 100 minutes of initial contact with Na-montmorillonite. The quinoline then continued to be sorbed and reached its equilibrium state after 4 days. Hamaker et al. (1967) reported that sorption of picloram increased for 23 days with no sign of having reached equilibrium.

The matter of reaching an equilibrium state is even more important when considering desorption proceeses. It has been shown that the longer a chemical has been in contact with sediment, the more difficult it is to desorb, which indicates a slow approach to equilibrium. In a study by Hamaker et al. (1966), it was found that, after an incubation period of 28 hours, picloram was much more difficult to remove from sediment than after an incubation of 2 hours. Meyers and Quinn (1973) took bentonite on which heptadecanoic acid had been sorbed and resuspended it in saline water, allowing desorption to occur. This process was repeated several times on the same bentonite, and the supernatant was analyzed after each suspension and desorption. Analysis showed that a smaller percentage of the acid retained on the bentonite was desorbed during each successive resuspension. Saba et al. (1969) also did desorption experiments with dieldrin sorbed on soil. They found that when dieldrin has been incubated for several months it is harder to extract from the soil than when it has been incubated for several days.

The different sorption rates and the fixation of organic chemicals on sediment is probably due to the concurrent action of two sorption mechanisms. Initially, there is a rapid physical sorption onto the organic sediment matter. Then, the chemicals diffuse more slowly into the interstitial clay (Saltzman and Yaron, 1971). Highly ionic material may have a higher affinity for the inorganic part of a soil or sediment than for the organic fraction. Burns and Audus (1970) sorbed paraquat which is highly ionic, on the separated organic fraction of a natural soil and suspended this in a dialysis bag. The bag was placed in a water suspension of the inorganic fraction of the soil. Within six hours, nearly all of the paraquat had moved through the dialysis bag and was sorbed onto the inorganic fraction. When the dialysis bag was suspended in distilled water, only 30% of the paraquat was released from the organic fraction.

8.8.7 Effect of pH on Sorption

Since different sediment-water suspensions frequently have different pH values, it is very important to know how pH of the system affects the adsorption characteristics. It is not expected that neutral compounds or strong acids and bases will be affected by changes in pH, because their form is not dependent on the pH of their environment. Weak acids and bases, however, can be present in two forms, depending on the pH of the environment. At low pH, weak acids are in the free acid form and weak bases are in the cationic form. Nearly all sediments have negatively charged sites; therefore, the free acid will be more highly sorbed than the anionic acid and the cationic base will be more highly sorbed than the free base. As the pH of the sorption system decreases the sorption of weak acids and bases increases. The pH dependency of adsorption has been demonstrated by several groups. Doehler and Young (1960) sorbed quinoline on various clay materials and found that quinoline sorption increased with decreasing solution pH. The solution pH was controlled by use of buffer solutions.

It has been shown that sorption increases rapidly as the pH approaches the pKa of the compound studied. Liu et al. (1970) studied the pH dependency of ametryne and diuron sorption and found that as pH decreased, sorption increased. At a pH approximately equal to the pKa, the sorption increased much more rapidly. Bailey et al. (1968) sorbed S-triazines, substituted ureas, and phenylalkanoic acid on montmorillonite clay and found that sorption began to increase at a surface pH about 1-2 pH units above the pKa and continued to increase as the pH further decreased.

The pH of a sediment-water system is difficult to determine because the pH of the solution can be different from the pH of the sediment surface. Bailey et al. (1968) observed that the pH of the sediment surface can often be 3-4 pH units lower than the solution pH. This conclusion was made by noting that very little atrazine should have been sorbed on the montmorillonite clay at the measured solution pH (due to little dissociation). Sorption, however, was almost complete, indicating that the pH of the clay surface must be about 3 pH units lower than the solution pH.

From the work done by Bailey et al. (1968), it would appear that the dependence of sorption on pH of the bulk solution or on pH of the sediment surface varies with different organic chemicals. They found that sorption of the basic S-triazines and substituted ureas depends on the surface acidity of the montmorillonite clay rather than on the pH of the bulk solution. For acidic compounds, (2,4-D), however, it was found that sorption was dependent on the pH of the solution. Unfortunately, very little other work has been done in this field, and any generalizations are made rather tenuously.

8.8.8 Effect of Other Dissolved Organics on Sorption

It is important to understand the effect of dissolved, indigenous organics on sorption of a particular organic chemical. Unfortunately, little work has been done in this area of research. It has been found, however, that organic chemicals are generally sorbed less when other dissolved organic chemicals are present. Meyers and Quinn (1973) performed experiments that involved removing various amounts of the indigenous organics from natural waters by sorption on filters. They used a Whatman-54 filter, which sorbs almost no organics, and a Gelman A filter, which removed almost all the organics. The treated natural water was then used for sorption isotherm experiments with heptadecanoic acid on bentonite. About 95% of the heptadecanoic acid was sorbed on the bentonite when the indigenous organics had been removed, and only about 85% was sorbed from the water still containing the indigenous organics.

The second experiment simulated sorptions onto marine sediments and involved equilibrating various organic chemicals in a saline solution before adding the fatty acids to be tested for sorption. After the fatty acids were mixed in, the clay was added. The organic chemicals used were glucose, amino acids, fatty acid methyl esters, fatty acids, soil fulvic acid, a synthetic mixture, and dissolved marine organic matter. They found that the presence of individual organics at naturally occurring levels did not significantly affect the fatty acid sorption. When combinations of organic chemicals were dissolved in the water, however, an appreciable decrease in sorption did occur. The significant decrease in sorption is due partly to the greater concentration of organics in the water for a mixture than for an individual organic chemical. Also studied in this experiment was the effect of allowing the fatty acids to "age" with the dissolved organics, before adding the sediment. An aging time of 24 hours resulted in a reduction in sorption 3 to 4 times greater than for an aging time of 15 minutes.

Decrease in sorption of organic chemicals when in the presence of other organic chemicals is apparently due to two mechanisms. The primary mechanism involves a change in solubility of the organic chemical when it is present with other organic chemicals. The water solubility of an organic chemical often increases when other dissolved organics are present, and sorption has been found to correlate inversely with solubility of an organic chemical in water (see Section 8.8.6).

The second mechanism that results in decreased sorption of an organic chemical when in the presence of other dissolved organics is competition for sorption sites. Indigenous organics will also be sorbed on the sediment particles and any sorption by them will decrease the number of sorption sites available to the organic chemical of interest. A decrease in sorption sites will result in decreased sorption.

8.8.9 Comparison of Using Wet and Dried Sediments for Isotherm Measurements

A factor affecting determination of sorption characteristics that has been largely ignored is the question of whether to use natural wet sediment suspensions or previously dried sediments. The character of the sediment is changed when it is dried. Some clays, such as montmorillonite have a lamellar structure, which when naturally wet holds a considerable amount of interstitial water. This interstitial water can affect sorption by altering access mechanisms to sorption sites.

Fulk (1975) has worked on determining if there are differences in pesticide concentration between the bulk solution and the interstitial water. No description was given for how the interstitial water was separated from the bulk solution. However, pesticide concentrations were much greater in the interstitial water than in the bulk solution. If this interstitial water were removed, the structure would collapse and access to sorption sites would be affected. Rewetting dried clay can be a difficult process. It may take several weeks for the system to equilibrate and the interstitial spaces to be filled with water so that they are once again in natural wet state.

Another important change that can occur in sediment when it is dried is the greater adhesion of any sorbed organics. If a sediment is dried, any organic chemical that has been sorbed on its surface will become more tightly bound. This is apparently due to the presence of water between the sediment and sorbed organic material when the system is in the naturally wet state. In dried sediment, the water layer is no longer present and the sediment-sorbate bond is strengthened. Graham and Bryce (1967), using disulfoton sorbed on soil, found that it was considerably harder to remove disulfoton from a dried and rewet sample than from a naturally wet sample.

A problem with storing wet samples is that biological degradation is likely to occur. Therefore, we recommend that the sediments be stored wet at 4°C to minimize biological activity and that they be used promptly.

8.8.10 Derivation of Equations

Equations (8.6), (8.7), (8.15), (8.25), and (8.27)

C_oV_c = Weight of chemical added to flask (μg)

$C_{ss}V_s$ = Weight of sediment added to flask (g)

F_s = Fraction of chemical sorbed

$C_oV_cF_s$ = Weight of chemical sorbed

$C_oV_c(1-F_s)$ = Weight of chemical in supernatant after equilibration with the sediment

$$C_s = C_oV_cF_s/C_{ss}V_s \qquad (8.25)$$

$$C_w = C_oV_c(1 - F_s)/V_t$$

then

$$C_s = (K_{oc}F_{oc})C_w = K_pC_w \qquad (8.5)$$

$$\frac{C_oV_cF_s}{C_{ss}V_s} = \frac{(K_{oc}F_{oc})C_oV_c(1 - F_s)}{V_t} \qquad (8.6)$$

and

$$V_s = \frac{F_sV_t}{(K_{oc}F_{oc})(1 - F_s)C_{ss}} \qquad (8.7)$$

Solving equation (8.6) for F_s, gives

$$F_s = \frac{(K_{oc}F_{oc})C_{ss}V_s}{V_t + (K_{oc}F_{oc})C_{ss}V_s} \qquad (8.15)$$

To satisfy the relationship that $V_s < (V_t - V_c)$, and solving equation (8.6) for C_{ss},

$$C_{ss} > \frac{F_sV_t}{(K_{oc}F_{oc})(1 - F_s)V_s} \qquad (8.25)$$

Equations for Centrifugation Time

The reader is referred to Ambler and Keith (1956) for a more general discussion of centrifuging. The force on a particle, expressed in grams, in a circle of rotation is

$$F = m\omega^2R/g \qquad (8.46)$$

where

F = centrifugal force (g)

m = mass of the particle (g)

ω = rotational velocity (radius sec^{-1})

R = radial distance from the particle to the axis of rotation (cm)

g = gravitational constant = 980.7 cm sec^{-1}.

Substituting the values of g

$$\omega = 2\pi N/60 \qquad (8.47)$$

where

$$N = \text{revolutions } (\text{min}^{-1})$$

into equation (8.46) gives

$$F = m(2\pi N/60)^2 R/980.1$$

$$= 1.117 \times 10^{-5} m\ R\ N^2 \qquad (8.48)$$

For convenience, the relative centrifugal force, RCF, is defined as

$$RCF = \omega^2 R/g \qquad (8.49)$$

which is the force acting on a particle in terms of multiples of its weight in the earth's gravitational field. Substitution of equation (8.46) into equation (8.49) gives

$$RCF = 1.117 \times 10^{-5}\ R\ N^2 \qquad (8.50)$$

The problem with using RCF is that it is directly proportional to R and the gravitational force on a particle increases as the particle moves to the end of the centrifuge tube. Therefore, the settling velocity will increase, and it is difficult to define the centrifugation conditions using equation (8.50).

Stokes law states that the viscous resistance to the motion of a small particle in a fluid is

$$F = 3\pi\eta D v_s \qquad (8.51)$$

where η is the viscosity of the fluid (in poise) and D is the diameter of the particle (cm). The mass of the particle in equation (8.46) must be corrected for the weight of the fluid displaced. Thus, for spherical particles, equation (8.46) becomes

$$F = (\pi/6)\ D^3\ \Delta\rho\ \omega^2 R \qquad (8.52)$$

where D is the diameter of the particle and $\Delta\rho$ is the difference of the density of the particle and the fluid ($\Delta\rho = \rho_p - \rho_\ell$).

Combining equations (8.51) and (8.52)

$$v_s = \frac{dR}{dt} = \Delta\rho\ D^2\ \omega R/18\eta \qquad (8.53)$$

For nonspherical particles,

$$v_s = \frac{dR}{dt} = \Delta\rho\ D^2\ \omega^2 RK/4\eta \tag{8.54}$$

where K is a shape factor and equals 2/9 = 0.222 for spherical particles. For nonspherical sediment particles, we used a value of $K = 0.15$.

Separating variables and integrating equation (8.54)

$$\int_{R_1}^{R_2} \frac{dR}{R} = \frac{\Delta\rho D^2 \omega^2 K}{4\eta} \int_o^t dt \tag{8.55}$$

$$\ln \frac{R_2}{R_1} = \frac{\Delta\rho D^2 \omega^2 K t_c}{4\eta} \tag{8.56}$$

and t_c, the identification time, in sec, is

$$t_c = \frac{4\eta\ \ln(R_2/R_1)}{\omega^2 D^2 \Delta\rho K} \quad \text{(sec)} \tag{8.57}$$

Since $\omega = 2\pi N/60$, equation (8.57) can be written

$$t_c = \frac{4\eta(60^2)2.303\ \log(R_2/R_1)}{(2\pi\ N)^2 D^2 \Delta\rho K} \text{ (sec)}$$

$$= \frac{840\eta\ \log(R_2/R_1)}{D^2 \Delta\rho K} \quad \text{(sec)} \tag{8.58}$$

If

$\eta = 0.0100$ poise at $20^\circ C$

$K = 0.15$

$\Delta\rho = \rho_p - \rho_\ell = 2.65 - 1.00 = 1.65$

$D = 2 \times 10^{-5}$ cm

then

$$t_c = \frac{840(0.01)\ \log(R_2/R_1)}{(2 \times 10^{-5})^2(1.65)(0.15)N^2}$$

$$= 8.48 \times 10^{10} \log(R_2/R_1)/N^2 \text{ (sec)}$$

$$= 1.41 \times 10^{9} \log (R_2/R_1)/N_2 \text{ (min)} \qquad (8.20)$$

Equation (8.21)

If only C_w is measured, then C_wV_t = weight of chemical in supernatant,

$$C_s = K_pC_w$$

$$= (C_oV_c - C_wV_t)/C_{ss}V_s \qquad (8.59)$$

$$K_p = (C_oV_c - C_wV_t)/C_{ss}V_sC_w \qquad (8.21)$$

8.8.11 Theory of Nonlinear Least Squares Estimates of Isotherm Parameters

Parameter estimates for the regression model described in Section 8.7.3 may be found using a Gauss-Newton algorithm to minimize the residual sum of squares. The BMDP3R program uses a modified version of the standard Gauss-Newton method, developed by Jennrich and Sampson (1977).

In the least-squares approach, the structural relation $y = f(\underset{\sim}{z}; \underset{\sim}{\Theta})$ is fit to observations Y_j, z_j, $j = 1,\ldots, n$, by finding $\underset{\sim}{\hat{\Theta}}$ such that:

$$S = \sum_{j=1}^{n} (Y_j - f(\underset{\sim}{z}_j;\underset{\sim}{\Theta}))^2 \qquad (8.60)$$

is minimized. Here, z_j is the vector of independent variables, and $\underset{\sim}{\Theta}$ is the vector of $m(m < n)$ parameters to be estimated. An observation is represented by the vector z_j and the value of the dependent variable, Y_j. For our application, $f(\underset{\sim}{z}_j; \underset{\sim}{\Theta})$ is given by

$$\hat{Y}_j = \sum_{i=1}^{p} \omega_{ij} \left[C_i(1 - \delta_j) + K_pC_i\delta_jM_s\right] \qquad (8.36)$$

where the notation is as described in Section 8.7.3.

Assuming that the function is twice differentiable with respect to each of the parameters, the least-squares estimate of $\underset{\sim}{\Theta}$ is the value $\hat{\underset{\sim}{\Theta}}$ that satisfies the system of m simultaneous equations:

$$\frac{\partial S}{\partial \Theta_i} = -2\sum_{j=1}^{n} (Y_i - f(\underset{\sim}{z}_j;\ \hat{\underset{\sim}{\Theta}})) \left.\frac{\partial f(\underset{\sim}{z}_j;\ \underset{\sim}{\Theta})}{\partial \Theta_i}\right|_{\hat{\underset{\sim}{\Theta}}} = 0; j = 1, \ldots, m \qquad (8.61)$$

In general, the equations will be nonlinear in Θ_i, and consequently, they may be analytically intractable.

The Gauss-Newton method is based on finding a particular sequence of vectors that converges to some limit L. This sequence is generated by the following scheme. From an initial estimate $\hat{\underset{\sim}{\Theta}}^{(0)}$ of $\hat{\underset{\sim}{\Theta}}$, the next vector in the sequence is generated by representing the function with a first-order Taylor series expansion:

$$Y = f(z;\hat{\underset{\sim}{\theta}}^{(0)}) + \sum_{i=1}^{m} \beta_i g_i \quad , \qquad (8.62)$$

where

$$g_i = \left.\frac{\partial f}{\partial \Theta_i}\right|_{\hat{\underset{\sim}{\theta}}} \quad \text{and} \quad \beta_i = (\hat{\Theta}_i - \hat{\Theta}_i^{(0)}).$$

This may be written as a linear function in the g_i's, and the coefficients β_i of the g_i's may be determined using ordinary least-squares regression. Then the next vector in the sequence, $\hat{\underset{\sim}{\theta}}^{(1)}$, may be generated by:

$$\hat{\Theta}_i^{(1)} = \hat{\Theta}_i^{(0)} + \lambda\beta_i \qquad (8.63)$$

where λ is chosen to be small enough that the residual sum of squares S decreases in stepping from $\hat{\underset{\sim}{\theta}}^{(0)}$ to $\hat{\underset{\sim}{\theta}}^{(1)}$. This procedure is repeated until a convergence criterion is met. The criterion is based on the relative reduction in the residual sum of squares from step to step.

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